

**FINAL REPORT -PHOTOASSISTED ELECTRON
TRANSFER REACTIONS -BERKELEY PIT WATER**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 3B**

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February 1998

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Transfer Reactions—Berkeley Pit Water**

**Mine Waste Technology Program
Activity IV, Project 3B**

Foreward

Industries are attempting to develop and modify their existing operations to manufacture products with environmentally-safe technologies. Wastes generated by these industries are often unsightly and can threaten public health as well as degrade the environment, especially if they are left untreated or are improperly treated. Mine wastes are particularly suspect because of the presence of “mobile toxic constituents” such as, for examples, cyanide that remains in tailings ponds and heap leach pads or acid mine drainage that contains heavy metals leached from sulfide minerals in exposed ore bodies.

The U.S. Environmental Protection Agency (U.S. EPA) is charged by Congress with protecting the nation’s land, air, and water resources. Under mandate of national environmental laws, the U.S. EPA strives to formulate and implement actions leading to a balance between human activities and nature’s ability to support and nurture life. Such laws direct the U.S. EPA to define environmental problems and thereby perform research, measure impacts, and find solutions. In this regard, the U.S. EPA’s National Risk Management Research Laboratory (NRMRL) is responsible for planning, implementing, and managing research, development and demonstration programs to provide an authoritative and defensible engineering basis in support of the U.S. EPA’s policies, programs and regulations with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities.

Similar responsibilities have also been assigned to the U.S. Department of Energy (U.S. DOE) through the Pittsburg Energy Technology Center (PETC), one of several U.S. DOE centers in charge of planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement was signed between U.S. EPA and U.S. DOE , IAG No. DW89935117-01-0, which made funds available to support the Western Environmental Technology Office (WETO) and their operating contractor, MSE Technology Applications, Inc. (MSE-TA), as well as Montana Tech of The University of Montana (Montana Tech) for the development of the Mine Waste Technology Program (MWTP).

The MWTP serves as a telecommunication and technology transfer center for the training and education of students (kindergarten through college) and professionals (K-12 teachers through mining representatives), a communication link that is vital to the general public’s understanding of the issues surrounding mine wastes and mining-related activities. Also, the MWTP funds projects for researchers to develop, demonstrate and/or implement technologies that solve environmental problems related to mine wastes and mining-related activities. Written reports of the projects are used to inform the user and professional communities and simultaneously complement the technology transfer facet of the MWTP. In this regard, workplans, quality assurance project plans (QAPP), and final reports on quality assurance/quality control (QA/QC) data are standard communications of the MWTP. The ensuing manuscript is a final report for presenting the QA/QC data that was obtained for MWTP Activity IV, Project 3B, “Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Berkeley Pitlake Water.” Project objectives were to identify and evaluate

appropriate technologies for using ultraviolet radiation to remediate Berkeley Pitlake Water, an acid-mine drainage system which contains dissolved heavy metals toxic to human life, via photooxidation and then to recommend whether follow-up research was needed or not.

Executive Summary

This final report presents QA/QC data obtained for MWTP Activity IV, Project 3B, “Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Berkeley Pitlake Water.” Several photoassisted electron transfer reactions were explored for the cleanup of mobile toxic constituents commonly found in mine wastewaters, in particular ferrous (Fe^{2+}), manganous (Mn^{2+}), arsenate (AsO_4^{3-}), and sulfate (SO_4^{2-}). Each of these reactions were photo-assisted involving electron transfer with solid photocatalysts and dissolved photosensitizers.

In this study, photo-oxidation experiments of Berkeley Pitlake water were conducted to remediate ferrous, manganous and arsenate ions with anatase (titanium dioxide, TiO_2) and hydrogen peroxide (H_2O_2) which are photochemical that were successfully used and demonstrated for the destruction of free and metal-complexed cyanide in MWTP Activity IV, Projects 3 and 3A (Ref. 1,2). Ferrous and manganous ions are expected to be removed by their oxidation to ferric and manganese(IV) and subsequent precipitation as oxy-hydroxides or other similar compounds. On the other hand, arsenate remediation is expected to occur via adsorption at the precipitate surface. In addition, photo-reduction experiments for sulfate remediation were conducted using strong reducing agents of sodium formate (NaCOOH) and hydrazine (H_4N_2) in the absence and presence of the anatase (TiO_2) in hopes of producing sulfide (S^{2-}) for the additional remediation of additional mobile toxic constituents such cupric (Cu^{2+}), zincic (Zn^{2+}), and cadmous (Cd^{2+}) cations via their precipitation as sulfide compounds. Research involving sulfate photo-reduction appears to be innovative since no published work on the method could be found. Reaction efficiencies were calculated and compared as remediation percentages for all experiments.

Results show that sulfate photo-reduction does work but, under the conditions examined, is not 100% effective. Photo-reduction the dissolved photochemicals proved to work best with hydrazine and formate yielding 9.2% and 6.7% remediation, respectively. When hydrazine and formate were used simultaneously with anatase, remediation percentages were observed to decrease to 5.4% and 2.9%, respectively. Anatase, by itself, only yielded 2.3% remediation. Consequently, it is concluded that the presence of anatase, as a solid photocatalyst, with either hydrazine or formate, as dissolved photochemicals, is detrimental to the homogeneous photolysis processes. Although sulfide formation was never observed, it is clear that photo-reduction of sulfate is possible with both homogeneous photolysis and heterogeneous photocatalysis. These promising technologies should therefore be examined in more detail in the near future.

By comparison, ferrous photo-oxidation could be 100% effective but is dependent on the conditions applied, especially pH. Results indicated that homogeneous photolysis with hydrogen peroxide worked better than heterogeneous photocatalysis with anatase: 28.8% remediation versus 6.1% remediation. Higher dosages of either photochemical yielded only marginal improvement in remediation. Further experiments showed that photolysis with hydrogen peroxide improved with decreasing wavelength, but was actually best in the absence of UV radiation. This surprising result was attributed to bubbling in

oxygen during the experiments as well as to not adding the photochemical continuously and observing a side reaction for only the UV-assisted experiments. The side reaction was attributed to photo-oxidation of organic species. Oxygen bubbling is believed to have created a mixed potential which lowered the solution potential (E_H) in the experiments below the potential required for manganous oxidation to occur. In this regard, manganous concentrations were not observed to change and its measurement was therefore removed from the critical list. Unfortunately, the selected pH condition of 3 was too low to observe adequate ferrous remediation. Iron concentrations in solution therefore remained high and interfered with the arsenic concentration measurement. In this regard, arsenic concentration was unable to be determined and its measurement was also removed from the critical list. Clearly, this photo-oxidation technology is promising but requires further study especially in regards to delineating the effect of pH, oxygen, continuous photochemical addition, and wavelength. The remediation of manganese via this technique would establish a process where the pH does not have to be adjusted to pH 11 as with the two-stage lime addition process which is, at this time, the best-determined available technology (BDAT). In this regard, this technique could eliminate the second stage and thereby yield substantial savings of lime.

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Acronyms and Abbreviations

A	acceptors
D	donors
EPA	U.S. Environmental Protection Agency
g/L	grams per liter
IC	ion chromatograph
ICP	inductively-coupled plasma
M	mole
ml	milliliter
Montana Tech	Montana Tech of the University of Montana
MWTP	Mine Waste Technology Program
nm	Nanometers
ppm	Parts per million
QA/QC	quality assurance/ quality control
S	photosensitizers
UV	Ultraviolet

1. INTRODUCTION

This final report was prepared from technical information and validated Quality Assurance/Quality Control (QA/QC) results obtained from Berkeley Pitlake water samples treated experimentally at Montana Tech of The University of Montana (Montana Tech) in Butte, Montana, for the Mine Waste Technology Program (MWTP), Activity IV, Project 3B - "Photoassisted Electron Transfer Reactions of Application to Mine Wastewater Cleanup: Berkeley Pitlake Water." All enclosed materials are follow-up to the approved MWTP Activity IV, Project 3B, Work Plan and Quality Assurance Project Plan (QAPP) dated June 1995 and May 1996, respectively (Ref. 3,4). The information and results are described in accordance with the requirements of the Interagency Agreement (IAG) Activity IV Scope of Work which was signed in June 1991 by the U.S. Environmental Protection Agency (U.S. EPA) and the U.S. Department of Energy (U.S. DOE) to initiate work on the MWTP. Furthermore, this MWTP final report addresses the testing and evaluation of a promising photolytic technologies for the remediation of mobile toxic constituents in mine wastewaters identified in MWTP Activity I Prioritization Reports (Ref. 5), Water and Acid Drainage.

1.1 Relevance to MWTP

Discharge waters from various municipal and industrial operations transport many dissolved chemicals that may have adverse effects on the environment of both plant and animal life. For example, dissolved chemicals may leach various heavy metals which would otherwise remain immobile. Aquatic life of all sorts can become sick or die due to the toxicity of both the dissolved chemicals and metals. Many wastewater processing technologies that are currently available or being developed consequently emphasize the removal of the dissolved chemicals as well as the heavy metals from the discharge waters. The remediation of the discharge waters has been considered paramount at several locations in Montana and throughout the United States (Ref. 5).

Impetus for this study emanated from the previous and successful studies on free and metal-complexed cyanide (Ref. 1,2) and from fundamental interests regarding the interaction of UV radiation (i.e. sunlight) with acid mine drainage systems such as the Berkeley Pitlake (Ref. 6). Further impetus comes from concerns of citizens near sites contaminated with acid mine drainage such as ARCO's and MRI's Berkeley Pitlake in Butte, Montana, where residents are concerned about the contamination entering their drinking (well) water especially after the Berkeley Pitlake reaches the critical water level. Similar problems have been noted for other sites in Montana and the United States (Ref. 5). In summary, photolytic technologies have been examined in this study and results are discussed in this final report for remediating Berkeley Pitlake water.

A Record of Decision (ROD) has been made which stipulates that lime precipitation is the Best Demonstrated Available Technology (BDAT) for remediating Berkeley Pitlake water (Ref. 7). However, because the critical water level of the Berkeley Pitlake will not be reached until 2021, the ROD also stated that a treatment plant did not have to operating until 2017 with construction beginning in 2013. This means there is over 15 years in which a better technology can be determined. In this

regard, a plethora of technologies have been and are presently being examined by the MWTP as part of Activity IV, Project 7 (Ref. 8). These technologies include The High Density Solids (HDS™) Process by Tetra Technologies, Inc. (Ref. 9), a silica gel chelation process by Purity Systems, Inc., (Ref. 10), an ion exchange process by Technical Assistance International, Inc., in conjunction with The Group of Russian Scientists (Ref. 11), a biosorption process with *Azolla* biofilter by SPC International and Hebrew University of Jerusalem (Ref. 12), and The Green Precipitate™ Process by Geo2 Limited (Ref. 13). Because one of the goals of this study was to develop a photolytic process for remediating Berkeley Pitlake water, it was not considered to be a demonstration project and consequently was submitted and later accepted as an Activity IV Project in which technologies are identified and evaluated (see Forward).

1.2 Research Objectives

The major objective of this project is to evaluate the effectiveness of photoassisted remediation of the mobile toxic constituents in the Berkeley Pitlake water, particularly iron and sulfate (as critical measurements) and arsenic and manganese (as non-critical measurements). Because iron and manganese are present in reduced states of +II, their remediation could be accomplished by photo-oxidation and subsequent precipitation of schwertmannite and pyrolusite, respectively. The photooxidation process would maintain the oxidation state of arsenic +V species and would convert any arsenic +III species to +V. Because arsenic +V species favor adsorption at iron precipitate surfaces, arsenic remediation would likely occur simultaneously with schwertmannite precipitation. On the other hand, because sulfate exists in a highly oxidized state (i.e., sulfur is +IV), its remediation can be accomplished by photo-reduction to sulfide and subsequent precipitation of heavy metal sulfides such as Cu^{2+} , Zn^{2+} and Cd^{2+} . Although somewhat negligible, some sulfate will be removed during schwertmannite precipitation. Through a proper selection of pH or redox (i.e., E_H) conditions, it would be possible to perform photoassisted remediation selectively. Other secondary objectives include examining direct photolysis, homogeneous photolysis, and heterogeneous photocatalysis to show feasibility, compare reaction efficiencies, and determine the effects of UV wavelength, reagent type, and reagent amount.

Because it is known that deep Berkeley Pitlake water (i.e., water taken from 200 feet or more below the surface) contains ferrous ion (Fe^{2+}), manganous ion (Mn^{2+}), arsenic predominantly as arsenate (AsO_4^{3-}), sulfur predominantly as sulfate (SO_4^{2-}) and a number of other elements as metallic cations or oxyanions, it will be clear from ensuing discussions in Section 2 that these species can be remediated by photolysis. The questions to be answered include (1) can ferrous be oxidized photolytically (i.e., photo-oxidized) to ferric and thereby induced to precipitate as ferrihydrite, (2) will the reaction be faster than with bubbled and dissolved oxygen as examined in previous studies (Ref. 14), (3) can arsenite photo-oxidize to arsenate simultaneously, (4) will resulting ferrihydrite precipitate adsorb, (5) will manganese behave similarly and thereby photooxidize to Mn^{4+} and simultaneously precipitate out as pyrolusite (MnO_2), and (6) can sulfate be photoreduced to sulfide (S^{2-}) which can then be recycled for precipitation of other mobile toxic constituents as sulfides such as Cu^{2+} , Zn^{2+} and Cd^{2+} as has been similarly demonstrated with sulfate-reducing bacteria, SRBs (Ref. 15-17). In this regard, other project

goals were to answer these questions and determine if the remediation can be accomplished selectively thereby demonstrating that a recovery process could be developed as opposed to a process which generates a sludge requiring disposal. Ultimately, it was hoped that a technology would be developed for sites where acid mine drainage occurs or, at least, be recommended for further study.

2. PHOTOCHEMISTRY

2.1 Technology Background

Remediation research of polluted waters originating from active or inactive mine sites and associated materials handling procedures has primarily focused on bringing to the affected areas foreign substances and processes which could ultimately disturb a naturally established ecosystem. Remediation methods by, for example, lime addition are inherently expensive and can make the sites difficult to revegetate. Overwhelming evidence shows that natural processes occur that heal environmental scars caused by mining activities. These processes include electron transfer reactions which lower the concentrations of mobile toxic constituents in surface and ground waters via interactions with electromagnetic radiation from the sun, ultraviolet (UV) radiation in particular. However, these naturally photoassisted processes suffer at night, on cloudy days, and in winter months. During these periods, artificial UV sources are needed to sustain the processes. Furthermore, because the processes may still proceed too slowly, photocatalysts or photosensitizers can be supplemented to absorb and transfer the UV radiant energy to the reactants thereby remediating the water within more acceptable time frames. Photocatalysts are predominantly solid semiconductors and photosensitizers are usually dissolved in solution.

In photolysis, solutions (or other sample types) are irradiated with electromagnetic radiation, usually UV, to promote electron transfer reactions between toxins (i.e., metal-complexed cyanide) and other available species. The toxins either undergo photoreduction or photooxidation to yield less toxic or non-toxic compounds depending on the reduction/oxidation (redox) chemistry of the system. Photolysis can be accomplished with direct or indirect techniques. Direct photolysis requires the substance being remediated to absorb the radiation. Indirect processes can be induced by having a second material absorb the radiation and then transfer the photo-energy to the substance being remediated. In this regard, solid semiconductors can be used such that they participate only as catalysts (heterogeneous photocatalysis). On the other hand, dissolved photosensitizers can either be consumed during the reaction (homogeneous photolysis) or participate as catalysts (homogeneous photocatalysis). These photoassisted processes are discussed below but, for simplicity, only as solid photocatalysis and dissolved photolysis.

2.1.1 *Solid Photocatalysis*

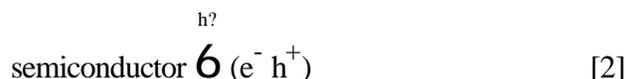
To date, most work has entailed studying the oxidation of toxic organic compounds using solid semiconductors as electron transfer photocatalysts to ultimately produce both carbon dioxide and water (Ref. 18-31). However, current emphasis appears to be on applying this successful technology to the remediation of inorganic compounds in order to satisfy new and more stringent environmental regulations including nitrate (Ref. 1,31-38), free cyanide (Ref. 1,38-56), metal-complexed cyanide (Ref. 2,50-60), and several metal cations (Ref. 18-20,26,35,44,49,54-65). Of course, it is the latter reports which are pertinent to this study; however it is important to illustrate that both photo-oxidation (e.g., cyanide) and photo-reduction (e.g., metal ions) is possible. Photo-reduction is less frequently observed presumably because the reducing power of the excited electron is significantly lower than the oxidizing power of the hole and because the compounds must kinetically compete with oxygen and/or

water as the electron acceptor (Ref. 25).

Numerous solid photocatalysts have been reported to work well: TiO₂, ZnO, WO₃, CdS, SiC, Fe₂O₃ and certain zeolites, to name a few. The anatase polymorph of TiO₂ has been preferred because of its low cost, relative abundance, and high quantum efficiency in converting photon energy into chemical energy (Ref. 39,40). In order for these solid semiconductors to function as electron transfer photocatalysts, their band gap energies must be less than the absorbed UV radiation as determined from the equation:

$$E = h\nu \quad [1]$$

where h is Planck's constant and ν is the frequency of the UV radiation. Upon absorbance, an electron is excited into the conduction band from the valence band where a "hole" is created (see Figure 2.1):



Because the band gap between the conduction and valence band edges lacks energy levels, the excited electron will reside at the conduction band edge whereas the hole will reside at the valence band edge. Consequently, the electron-hole ($e^- h^+$) pair will be relatively stable possessing a lifetime that is long enough for electron transfer reactions to occur:



Clearly, electron donors (D) become oxidized when they release electrons to fill the holes (Reaction 3) and electron acceptors (A) are reduced when they consume the excited electrons (Reaction 4).

Solid electron transfer photocatalysis can not occur unless both A and D are preadsorbed at the semiconductor surface and the products, D^+ and A^- , do not react with respective excited electrons and holes to reproduce the reactants. Otherwise no net reaction results. Furthermore, the Nernst potentials of Reactions 3 and 4 must be thermodynamically favorable. Each of these requirements can be met by (1) using semiconductors that are amenable to the adsorption of both A and D but not A^- and D^+ , (2) choosing a semiconductor whose band gap is appropriate for the electron transfer reactions to occur, (3) choosing ligands which react with the radical products to form inert species, (4) selecting appropriate pH conditions, (5) stirring/bubbling the system to remove the radical products from the surface, (6) promoting reactions between the radical products themselves, and (7) depositing metals (i.e., platinum) at the surface as a co-catalyst to localize the excited electrons. Clearly, the surface, electro-, solution, and analytical chemistries of the solid electron transfer photocatalytic reactions must be well understood before they can be induced and/or enhanced. It is important to note that platinum-deposition is accomplished by the photo-reduction of platinum in solution using an appropriate

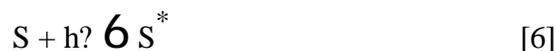
photocatalyst which essentially is the same as remediating platinum from solution (Ref. 64,65)!

2.1.2 Dissolved Photolysis

Photochemical reactions in the absence of solid semiconductors have involved both organic and inorganic compounds and have been classified as either direct or indirect processes. In direct photochemical processes, the compound (designated as X in subsequent equations) absorbs the electromagnetic radiation to form an excited state which then reacts to form a variety of products (see Figure 2.2):



For most organic compounds, this reaction is typical of a decomposition reaction. For certain inorganic compounds, this reaction either (1) yields changes in oxidation states or (2) transfers the photo-energy to water yielding hydroxyl radicals (OH^*) which can then decompose various organic compounds or react with other inorganic species to produce specific radicals (Ref. 18-21,39,61). With indirect photochemical processes, photosensitizers absorb the radiation



and then transfer the photo-energy to the compound thereby catalyzing the following reaction:



or transfer the energy to another species (usually oxygen) to induce the following reactions:



where the oxygen radical may participate as either a reactant or a co-catalyst. In some cases, the photosensitizer (S) is consumed in the process and is therefore not considered to be a dissolved photocatalyst.

Each of the radicals mentioned above (i.e., inorganic, organic, hydroxyl, specific, photosensitizer, and oxygen) are dissolved photocatalysts and can induce oxidation (electron donating) or reduction (electron accepting) reactions in the same manner as solid photocatalysts. However, the dissolved photocatalysts are not dependent on adsorption and other surface area phenomenon and, by comparison, can therefore be expected to enhance reaction rates by orders of magnitude, dependent only on the concentration of the dissolved photocatalyst. Other dissolved photocatalysts include photon-active redox couples where the oxidant would be the electron donor and the reductant would

be the electron acceptor.

2.2 E_H-pH Diagrams

Because photolysis involves electron transfer reactions, it is helpful to examine thermodynamic equilibrium diagrams such as E_H-pH diagrams to see what possible reactions may occur between reacting species and to see what products may be formed as the reaction occurs. In this regard, E_H-pH diagrams were generated using STABCAL (Ref. 66,67) and shown to be very reliable in previous and other ongoing MWTP projects (Ref. 1,2,68-71). STABCAL is a program developed for IBM-compatible personal computers to calculate various types of thermodynamic stability diagrams. In order to construct the diagrams for iron, arsenic, manganese, sulfate and anatase, thermodynamic data at 298K was obtained from NBS tables using a reference library within the STABCAL program (Ref. 72).

At the 200-foot depth of the Berkeley Pitlake (i.e., deep Berkeley Pitlake water) where samples are often collected for research purposes, E_H-pH conditions typically measure 0.6 volts (E_H) and 2.65 (pH). These conditions are marked with a star on each of the ensuing E_H-pH diagrams.

2.2.1 Iron Photo-Oxidation

The E_H-pH diagram for the iron-water system in Figure 2.3 confirms that the predominant iron species for deep Berkeley Pitlake Water is aqueous ferrous cations (Fe²⁺). However, if the conditions are perturbed via UV irradiation and, if necessary, the addition of a photochemical, the ferrous cation can be oxidized to ferric cation by, for example, reacting with a hole, h⁺:



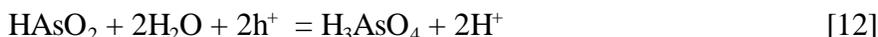
Because ferric cations are relatively unstable in water, an immediate reaction with water or dissolved oxygen will occur in which hematite (Fe₂O₃), or other similar iron species such as ferrihydrite [Fe(OH)₃], will precipitate:



The iron-precipitate can be easily removed via conventional solid/liquid separation processes such as thickening and filtering. However, because Berkeley Pitlake water contains sulfate at high concentrations, it is most likely that, under the conditions of deep Berkeley Pitlake water, ferrous sulfate [FeSO₄(aq)] is the predominant iron species and schwertmannite [Fe₈O₈(OH)₆SO₄·5H₂O] is the likely precipitate that will form upon photooxidation (Ref. 73,74). This is illustrated in the E_H-pH diagram for the iron-sulfur-water system in Figure 2.4 and is similar to the iron-water system in Figure 2.3.

2.2.2 Arsenic Photo-Oxidation

An E_H -pH diagram for the arsenic-water system is illustrated in Figure 2.5. The dihydrogen arsenate ion ($H_2AsO_4^-$) is depicted to be predominant arsenic species under the conditions noted for deep Berkeley Pitlake water. However, because deep Berkeley Pitlake water conditions are near the stability region of arsenious acid ($HAsO_2$), it is likely that arsenious acid will be present in minor amounts. Nevertheless, arsenious acid will convert to arsenate ion in the presence of UV radiation and an appropriate photochemical (Ref. 75):



This is significant for two reasons: all arsenic species would be present as As (V) and As (V) species are easier to remove from solution than As (III), especially if the ferrihydrite adsorption method is used (Ref. 76-78). Consequently, arsenic remediation can be conducted simultaneously with the ferrous photooxidation process described above (see Reactions 10-11).

2.2.3 Manganese Photo-Oxidation

An E_H -pH diagram for the manganese-sulfur-water system is shown in Figure 2.6. It confirms that the predominant manganese species under the conditions of deep Berkeley Pitlake water is manganous cation (Mn^{2+}). Like iron, manganous cations can also photo-oxidize to form a precipitate:



The precipitate of pyrolusite (MnO_2) can also be removed by conventional solid/liquid separation techniques. It is not known whether manganese will form a precipitate similar to schwertmannite due to the presence of sulfate in the Berkeley Pitlake water. Nevertheless, manganese removal from acid mine waters can be conducted simultaneously with iron and arsenic removal or selectively if appropriate redox potentials can be maintained.

2.2.4 Sulfate Photo-Reduction

Because of the presence of sulfate in the Berkeley Pitlake water, the E_H -pH diagram in Figure 2.7 for the sulfur-water system was previously superimposed on Figures 2.4-2.6 for the iron-, arsenic- and manganese-sulfur-water systems, respectively. However, in order to remediate sulfate by photolysis, a reduction reaction involving photon-excited electrons must be induced to yield elemental sulfur (S^0) or aqueous hydrogen sulfide (H_2S):



Although elemental sulfur could be removed via conventional solid/liquid separation techniques, its formation is unlikely due to a large activation energy barrier that must be overcome and consequently leads to the production of aqueous hydrogen sulfide (Ref. 79,80). In this regard, elemental sulfur was

not included in any of the previous E_{H} -pH diagrams (see Figures 1.4-1.6). Nevertheless, aqueous hydrogen sulfide could be used directly or converted to a gas for recycling and precipitation of other heavy metals (e.g., Cu^{2+} , Zn^{2+} and Cd^{2+}) in the Berkeley Pitlake water (Ref. 9,68). A similar approach to this is the use of sulfate-reducing bacteria to produce sulfide (Ref. 15-17). Conventional solid/liquid separations could then be used to process the sulfide precipitates.

2.2.5 Anatase Photocatalysis

Reactivities for electron-hole pairs produced at anatase (TiO_2) surfaces were superimposed on the E_{H} -pH diagram presented for the iron-water system in Figure 2.3. For clarity, the reactivities were not shown for iron-sulfur, arsenic-sulfur, manganese-sulfur, and sulfur-only E_{H} -pH diagrams in Figures 2.4-2.7. A comparison of Figures 2.1 and 2.3 shows that the valence and conductance bands are reversed; however, this is merely due to convention. The position of the bands concurs with those determined at pH 1, 7, and 14 and illustrates that the bandgap for anatase is 3.2 eV (Ref. 18-20,61). According to Equation 1, a photon must have a frequency of 7.75×10^{14} Hz in order for its absorbance to occur. This equates to a maximum wavelength of 387.5 nm and therefore indicates that the various UV sources employed in this study were adequate for inducing solid photocatalysis (see Section 3 - Treatability). As previously noted, conductance and valence bands represent the affinity for electrons to be consumed (by holes) and donated (as excited electrons) and are therefore a measure of relative reduction and oxidation potentials, respectively. Because ferrous and manganous cations as well as arsenous acid lie below the valence band, they can be expected to undergo oxidation, as depicted in Reactions 10 through 13, by releasing electrons to photon-produced holes. Similarly, since sulfate species lie above the conductance band, it can be expected to undergo reduction, as depicted in Reaction 14, by accepting photon-excited electrons.

2.3 Preliminary Investigations

Two preliminary investigations to this QA/QC study were conducted separately; the first by Steve Cashin led to the initiation of this MWTP Acitivity IV Project 3B (Ref. 81), and the second by Yu-Chuan Tai resulted in his thesis (Ref. 82) as well as the QA/QC results (see Section 3).

2.3.1 Cashin and Young

Preliminary data obtained previous to this investigation by Cashin and Young (Ref. 81) for iron remediation from Berkeley Pitlake water in the absence and presence of UV radiation and a photolytic reagent (i.e., H_2O_2) is shown in Figure 2.8. These results were obtained by stirring 200 ml of Berkeley Pitlake water under open conditions. The best results are observed to occur when the photolytic reagent was used and exposed to UV radiation for 240 minutes. The iron concentration in the Berkeley Pitlake decreased from approximately 1300 ppm to nearly 620 ppm due to Fe(II) oxidation and subsequent precipitation of an Fe(III) species such as hematite, ferrihydrite or schwertmannite (see Reactions 10 and 11a,b). This equates to a

remediation value of 52%. By comparison, only 42% iron remediation was observed in the absence of UV radiation (i.e., dark). Clearly, these exciting results led to a thesis (Ref. 82) and the study reported in this final report.

It is important to note that iron oxidation in the absence of a photolytic reagent could be achieved simply by stirring in open air and reacting with molecular oxygen. However, reaction times are shown to be very slow in agreement with the literature (Ref. 68). Interestingly, equilibrium results were obtained more quickly in the presence of UV radiation. This direct photolytic process suggested that sunlight may play a significant role in acid mine drainage systems. This conclusion has given rise to a future study on naturally-occurring reactions in the surface waters of the Berkeley Pitlake (Ref. 6).

Cashin and Young (Ref. 81) also examined the concentrations of other metals during these preliminary iron oxidation experiments. Results for Mn, Al, Cd, Cu and Zn are shown in Figures 2.9 through 2.13, respectively. Mn as shown in Figure 2.9 appears to behave like Fe. Examination of the E_H -pH diagram for Mn suggests Mn²⁺ photo-oxidized to Mn⁴⁺ and precipitated out as MnO₂ as discussed earlier (see Figure 2.6 and Reaction 13). By comparison, E_H -pH diagrams for Cu, Zn, Al, and Cd in the literature (Ref. 83,84) show that increased oxidation potentials caused by photolysis of H₂O₂ should not affect their solution concentrations. The results obtained for Al and Cd in Figures 2.10 and 2.11 appear to verify this hypothesis. However, the results for Cu and Zn in Figures 2.12 and 2.13 appear to as well but only in the presence of UV radiation. This behavior is explained by Cu and Zn adsorption at the surface of the Fe and Mn precipitates in the absence of UV radiation. In the presence of UV radiation, interfacial phenomena, perhaps induced by the formation of holes and excited electrons at the precipitate surfaces due to photocatalytic properties, prevent their adsorption. In this regard, the behavior of Al and Cd is tentatively referred to UV-independent adsorption and the behavior of Cu and Zn is referred to as UV-dependent adsorption. Based on these results and the possibility of using sunlight as a free source of UV radiation, it is understandable how these preliminary results led to this investigation.

2.3.2. *Tai and Young*

As part of his thesis (Ref. 82), Tai conducted a series of experiments in the absence and presence of UV radiation to examine the effect of pH on H₂O₂ photo-oxidation of Berkeley Pitlake water. The pH was adjusted with NaOH instead of lime to avoid gypsum precipitation. Results are presented in Figures 2.14 and 2.15 with and without 254nm UV radiation, respectively.

Figure 2.14 shows Fe is preferentially precipitated at pH values less than 4. At higher pH values, both Cu, Zn, and Al concentrations begin to decrease due to metal-hydroxide formation and/or adsorption at the surface of the iron precipitate. Mn and Cd concentrations are relatively constant until pH values exceed 6. Since Mn was not remediated, the results contrast with those obtained by Cashin and Young (Ref. 81). The reason for this behavior was not determined until QA/QC experiments were conducted (see Section 3.2 - Experimental Results). All other results presented in Figure 2.14 appear to concur with those of Cashin and Young (Ref. 81) as do most of the results presented in Figure 2.15.

Figure 2.15 shows that, in the absence of UV radiation, both Cu and Al are remediated from solution at pH values greater than pH 3. Because Cu and Al exhibit different concentration profiles (compare Figures 2.14 and 2.15), their behavior is attributed to adsorption. On the other hand, the concentration profiles of Zn and Cd as a function of pH appear to be independent of UV exposure. Their pH profiles can therefore be attributed to precipitation. By comparison, the Mn-profile is relatively independent of pH and thus does not exhibit either adsorption or precipitation behavior; hence, the importance of remediating Mn via (photo-)oxidation in order to avoid a 2-stage lime precipitation process.

It was therefore concluded that selective iron removal from Berkeley Pitlake water could be accomplished but, presumably, would require UV radiation to prevent or minimize Cu and Al adsorption and, more importantly, would require pH values to be below pH 4. Consequently, in order to examine the effects of UV radiation on iron without changing the concentration of the other metals, it was decided that QA/QC experiments should be conducted at pH 3 (see Section 3.1 - General Test Procedures).

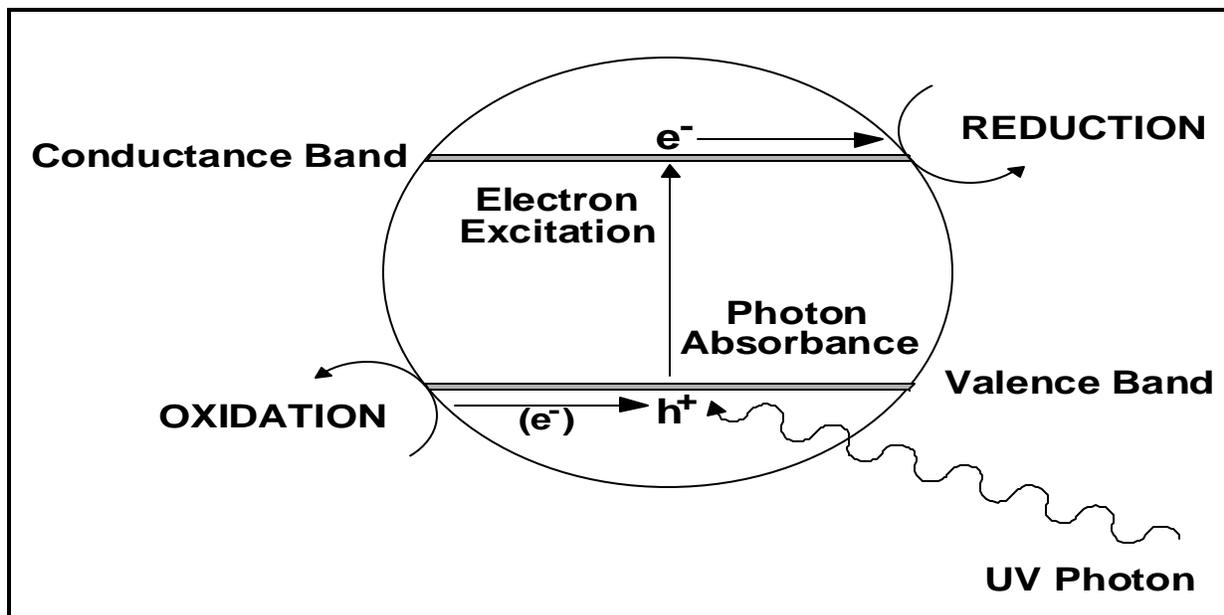


Figure 2.1. Schematic of the photocatalytic process for

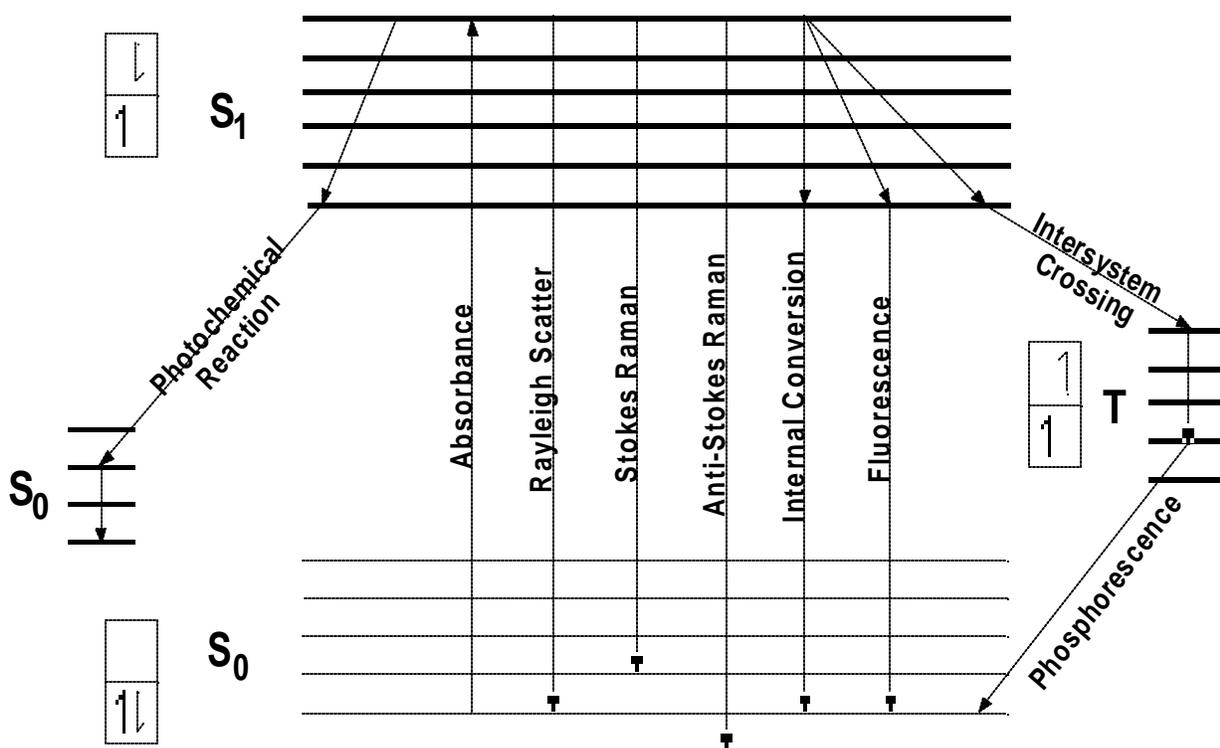
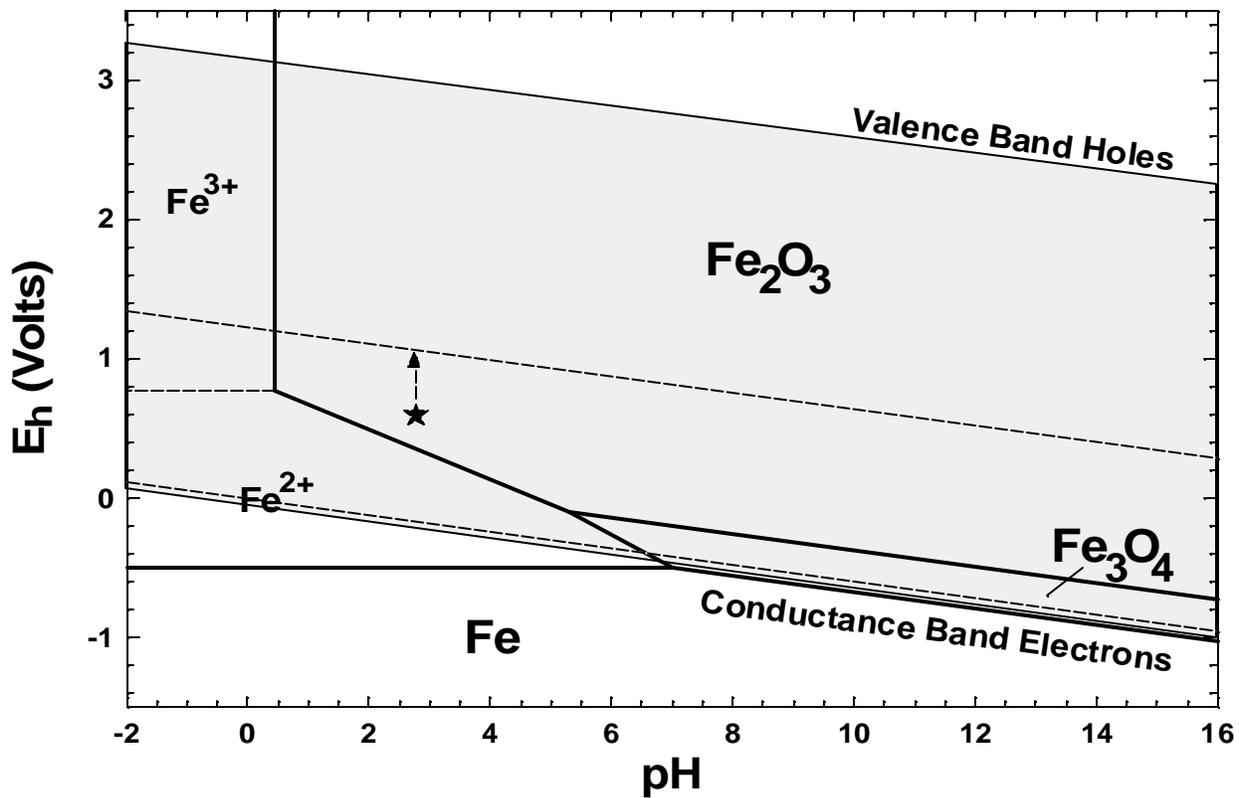


Figure 2.2. Jablonski energy level diagram depicting the various relaxation pathways an electron after being excited by photon Figure



2.3. E_H -pH diagram for the iron-water system at 298 K.

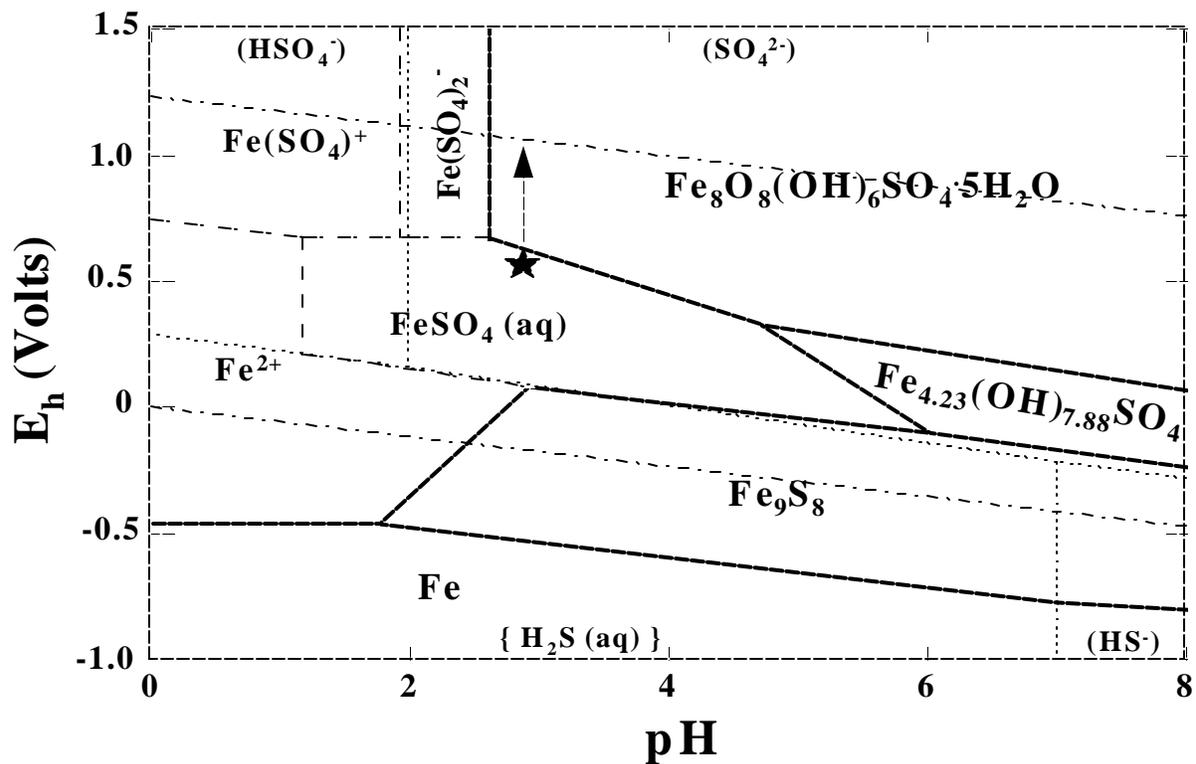


Figure 2.4. E_H -pH diagram for the iron-sulfur-water system at 298 K.

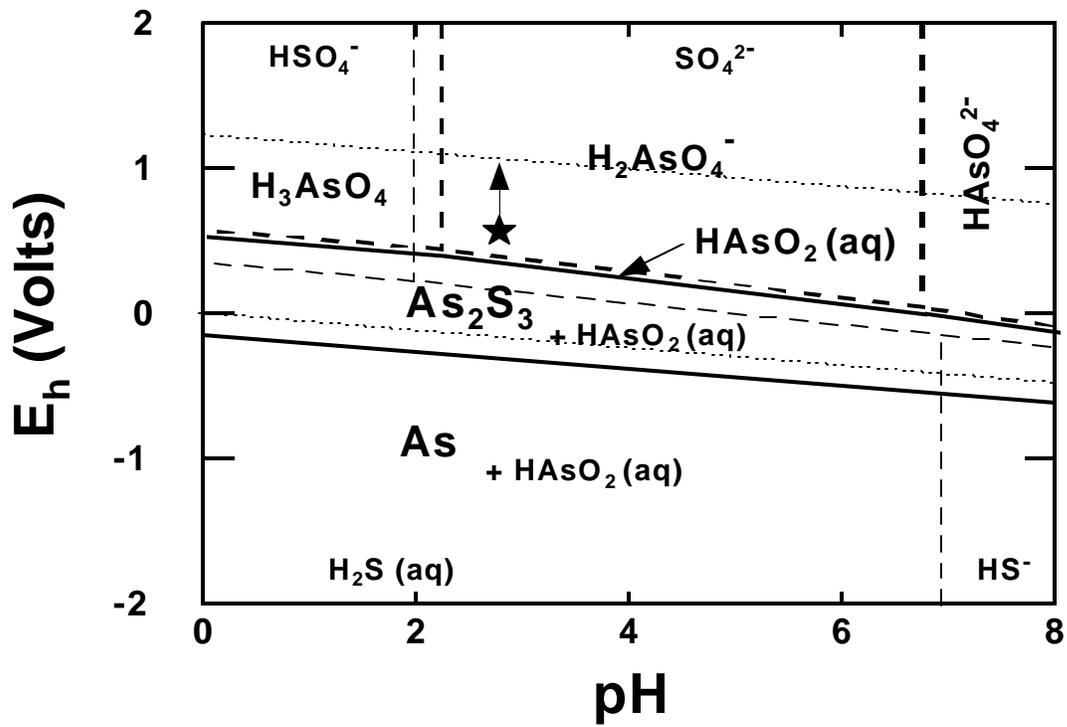


Figure 2.5. E_H -pH diagram for the arsenic-sulfur-water system at 298 K.

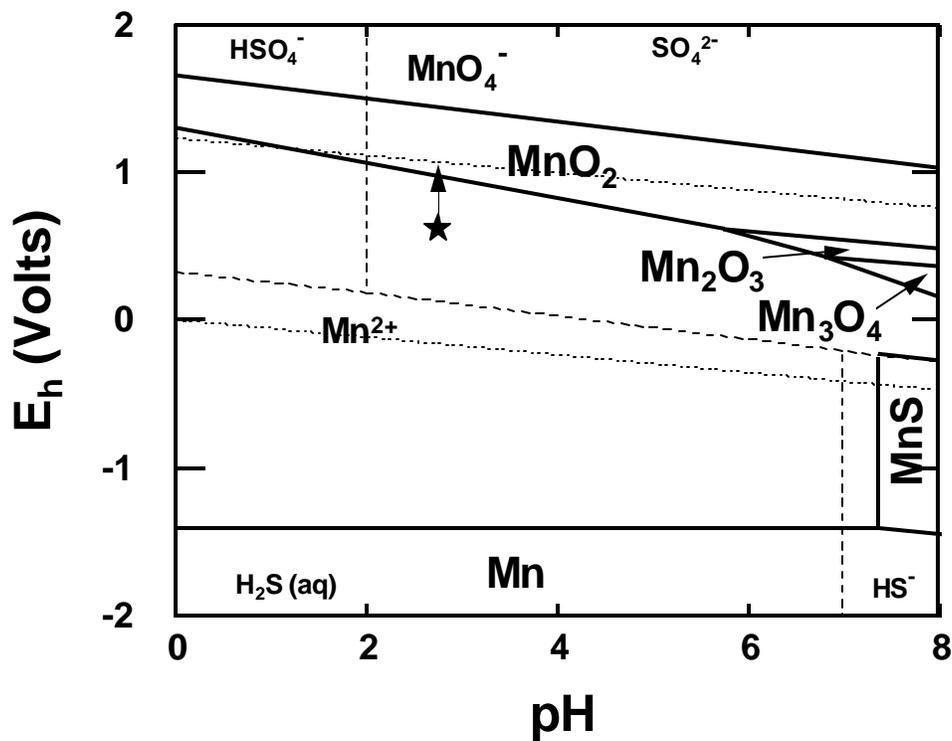


Figure 2.6. E_H -pH diagram for the manganese-sulfur-water system at 298 K.

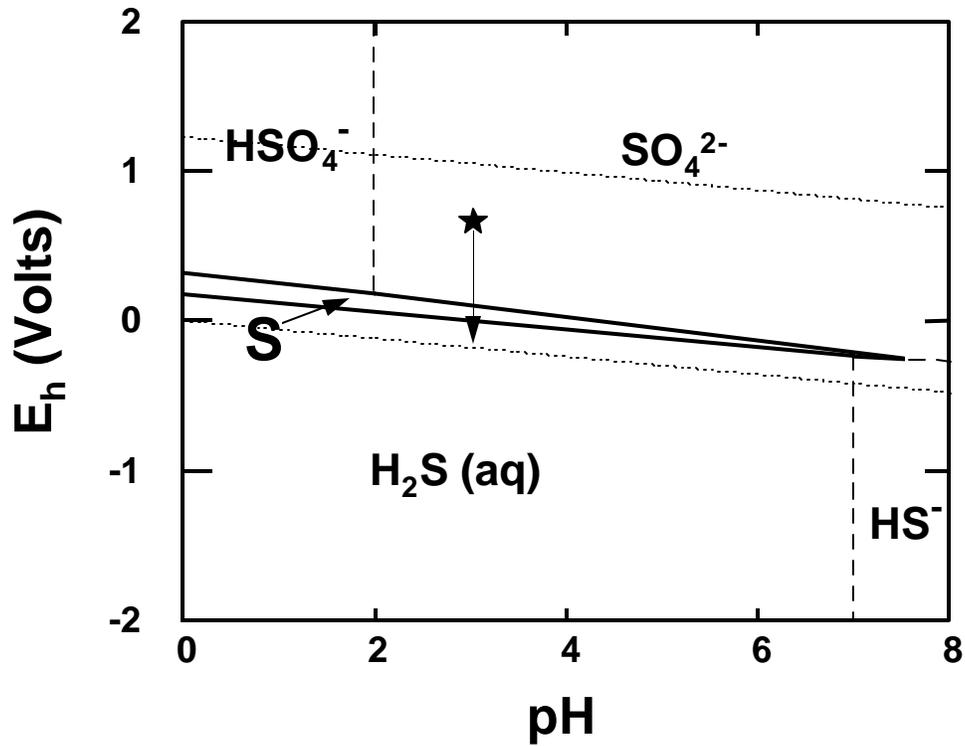


Figure 2.7. E_h -pH diagram for the sulfur-water system at 298 K.

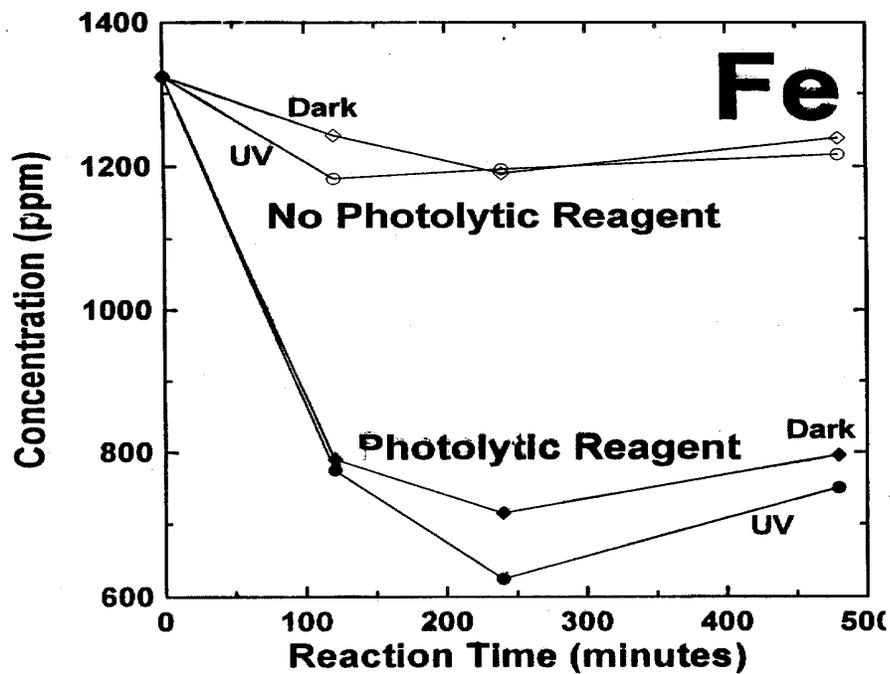


Figure 2.8. The effect of a photolytic reagent and UV irradiation on iron remediation as a function of time.

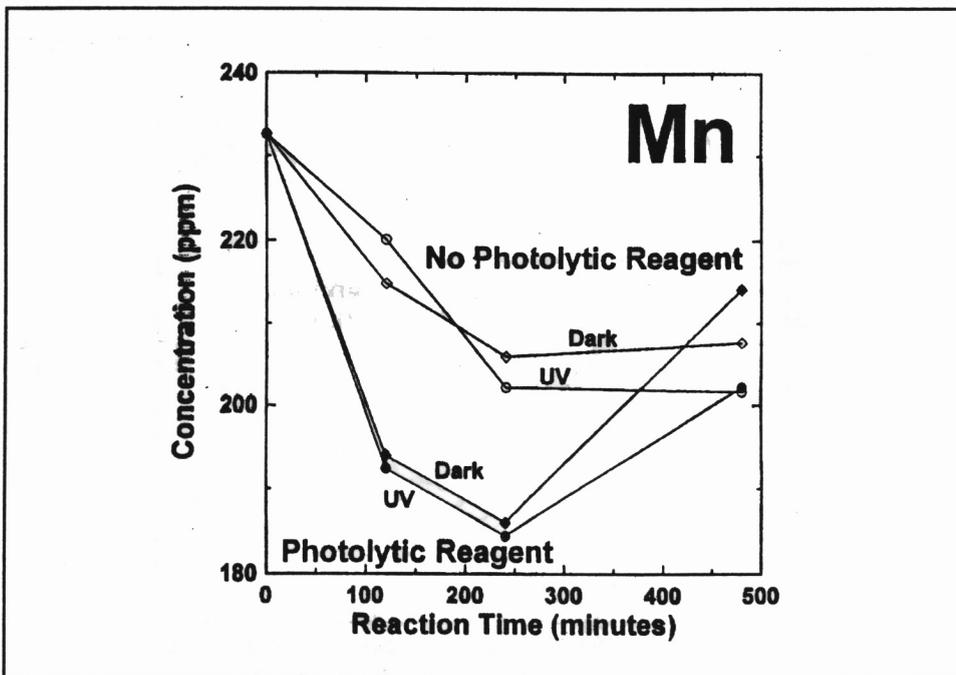


Figure 2.9. The effect of a photolytic reagent and UV irradiation on manganese remediation as a function of time.

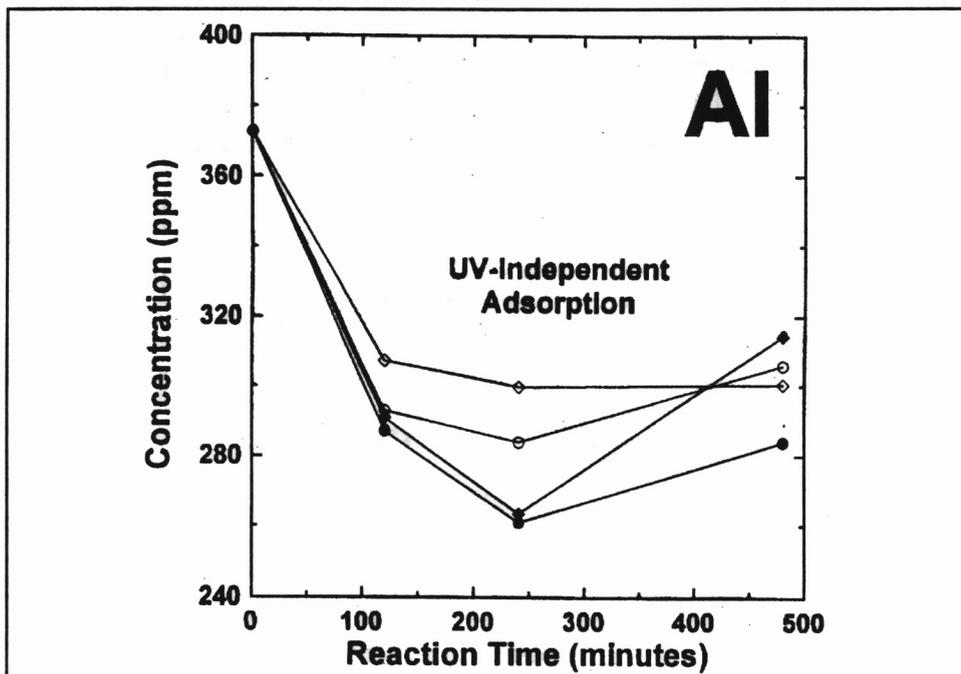


Figure 2.10. The effect of a photolytic reagent and UV irradiation on aluminum remediation as a function of time.

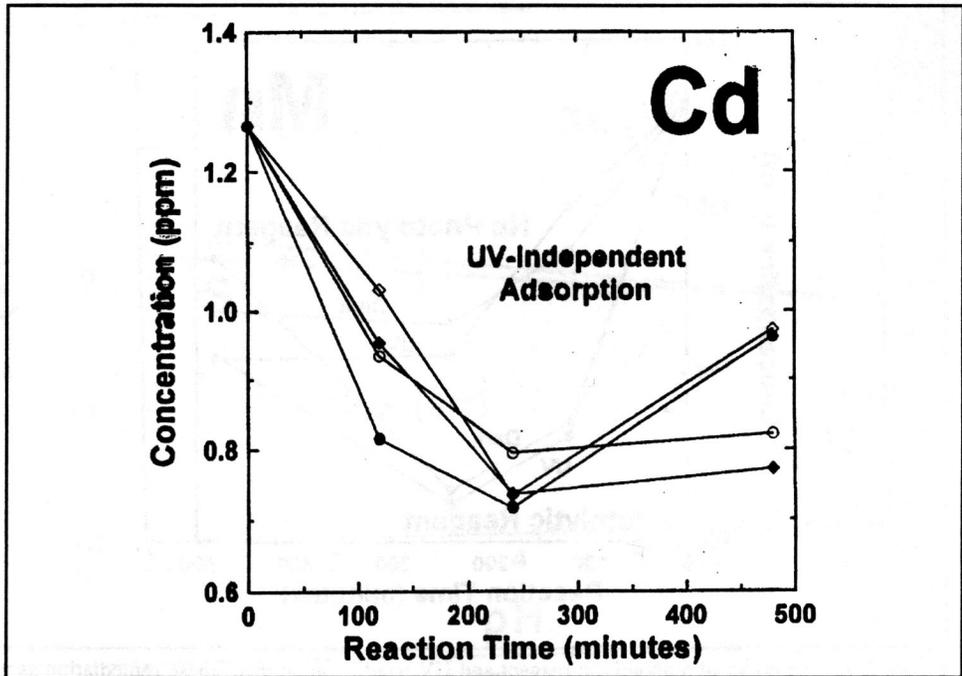


Figure 2.11. The effect of a photolytic reagent and UV irradiation on cadmium remediation as a function of time.

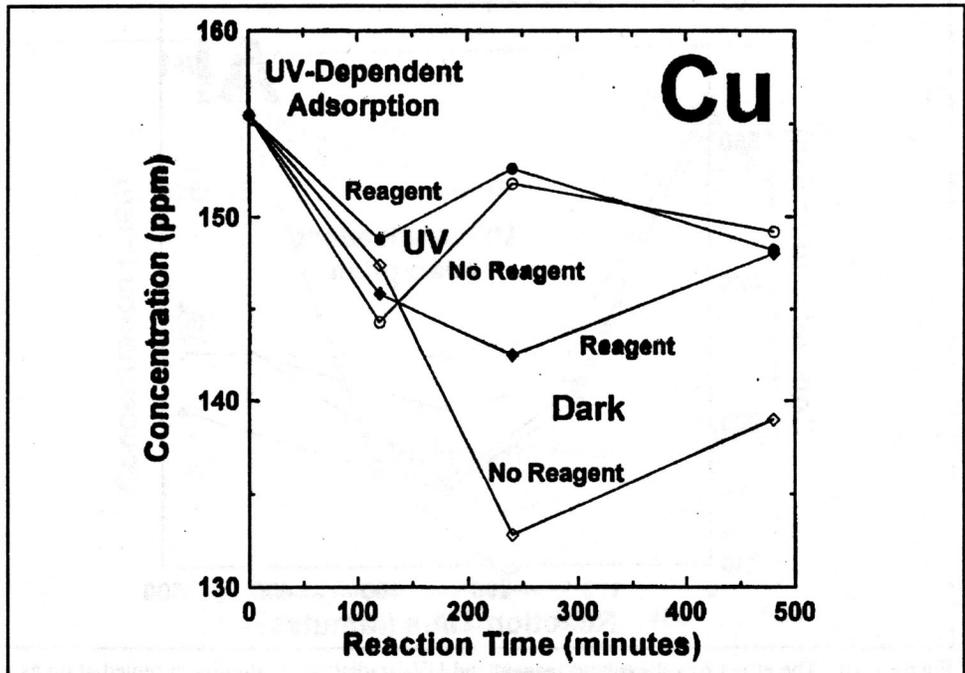


Figure 2.12. The effect of a photolytic reagent and UV irradiation on copper remediation as a function of time.

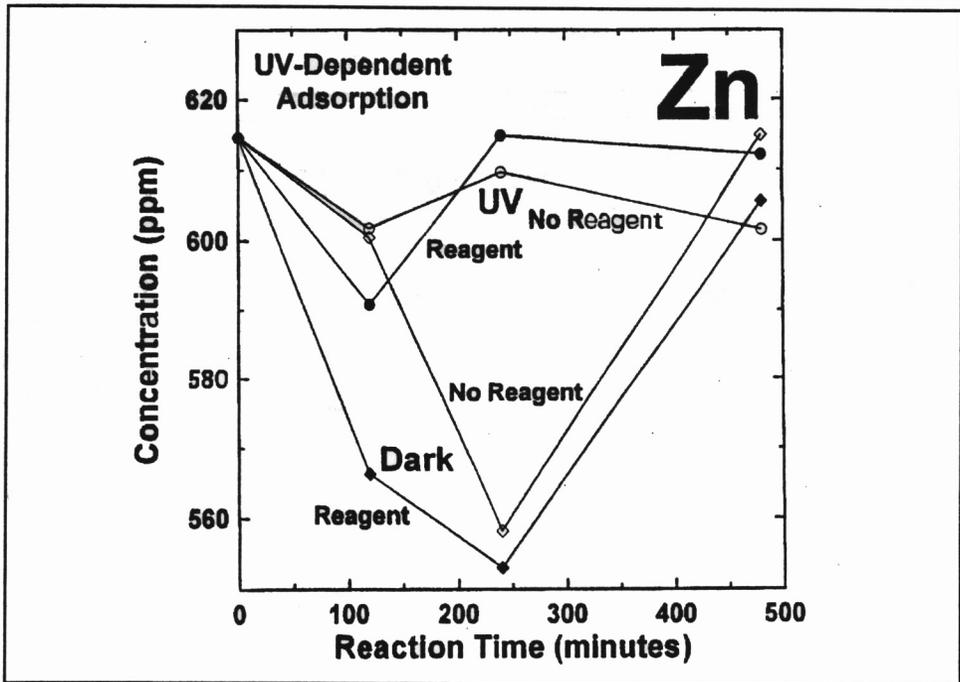


Figure 2.13. The effect of a photolytic reagent and UV irradiation on zinc remediation as a function of time.

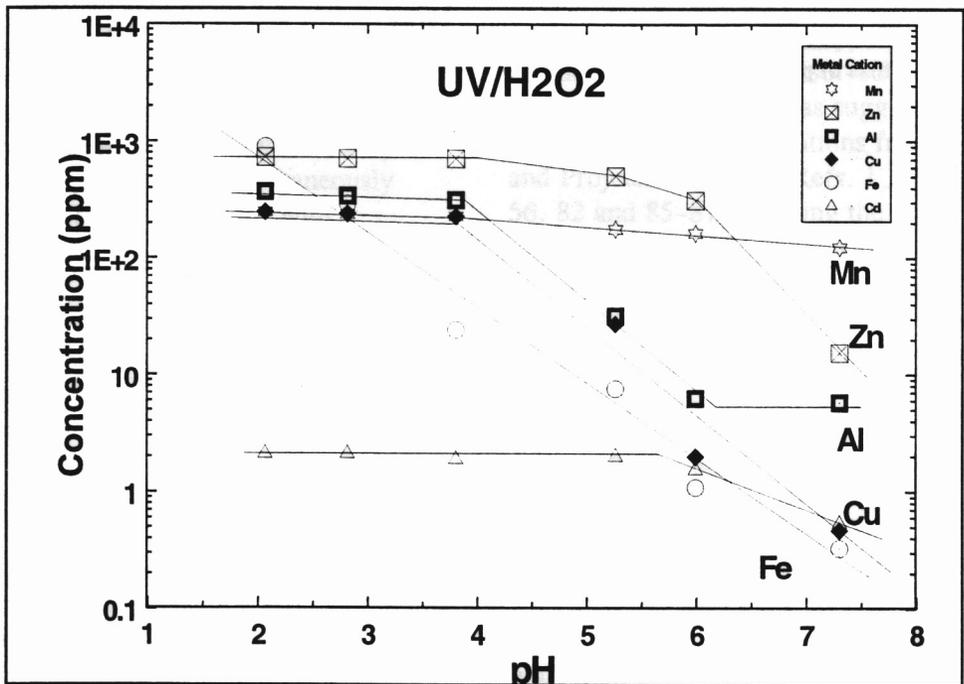


Figure 2.14. Effect of pH and H₂O₂ photo-oxidation on heavy-metal remediation of Berkeley Pit water.

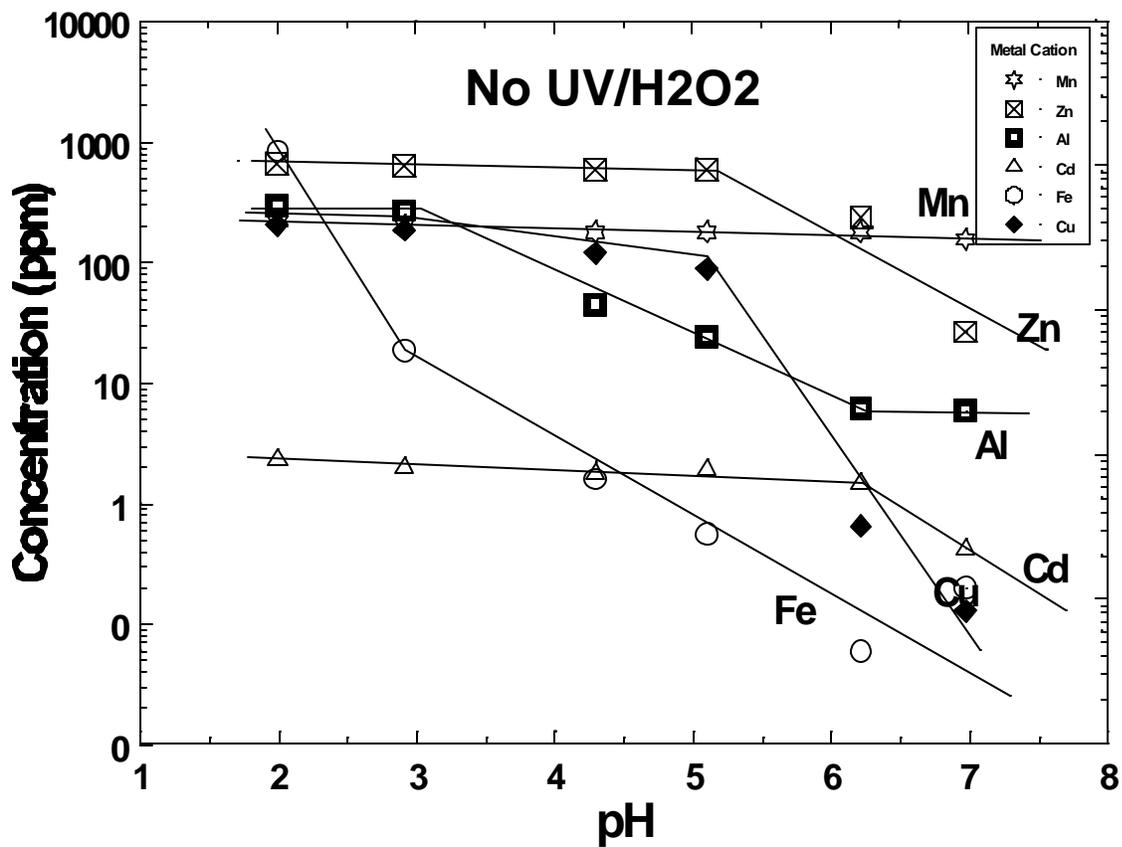


Figure 2.15. Effect of pH and H₂O₂ oxidation on heavy metal remediation of Berkeley Pitlake water.

3. TREATABILITY

Experimental procedures were the same in this study as for the photooxidation experiments of free cyanide and metal-complexed cyanide and photo-reduction experiments of nitrate conducted in the previous MWTP studies (Ref. 1,2). A major difference was how the mobile toxic constituents were detected and quantified. In this regard, an inductively-coupled plasma (ICP) spectrophotometer was used.

3.1 General Test Procedures

For this project, a 5-gallon sample of water from the Berkeley Pitlake was collected and transported to the ELC Building at Montana Tech by the Montana Bureau of Mines and Geology. The water was obtained from the 200-foot depth (i.e., deep Berkeley Pitlake water) and stored in a refrigerator to help maintain freshness (see Section 6 - Field Samples). Aliquats measuring 150 milliliters (ml) were taken from this sample for each experiment and placed in standard 250 ml Pyrex beakers (Fisher) as reaction vessels. The aliquats were magnetically stirred using the experimental setup shown in Figure 3.1. The experimental set-up shows the pyrex beaker being illuminated by a UV source from above while simultaneously being sparged by a gas and stirred magnetically with a magnetic stirrer and Teflon-coated stirbar (VWR). The magnetic stirrer was operated at approximately 2-speed.

Experiments were conducted in the absence and presence of both UV radiation and photochemicals. The UV sources (Rayonet) had rated intensities of 16000 FW/cm² and emitted radiation with peak intensities at wavelengths of 185, 254 or 365 nm. Photochemicals included hydrogen peroxide (J.T. Baker), hydrazine hydrate (J.T. Baker), sodium formate (Fischer), and anatase (Degussa P25). De-ionized/distilled water was used for the dissolution of photochemicals prior to their addition, and the dilution of acid (H₂SO₄ or HNO₃, J.T. Baker) and base (NaOH, Fischer) for pH control. All reagents were reagent grade and obtained from the indicated commercial manufacturers. Most photo-oxidation experiments involving iron, arsenic and manganese remediation were continuously sparged with oxygen gas (General Distributing Co.) to maximize oxidizing conditions and were conducted at pH 3. All photoreduction experiments involving sulfate were continuously sparged with argon gas (General Distributing Co.) to maximize reducing conditions and were conducted at pH 6. Gas flow rates were measured with an in-line flow meter. Experiments were conducted for 1.5 hours. Non-irradiated tests would help ascertain the applicability of photolysis.

QA/QC was conducted at all times (see Ref. 4 as well as Section 4 - Quality Assurance/Quality Control; and Section 6 - QA/QC Activities). Experimental conditions for the 11 photo-oxidation, 5 photoreduction, and 5 non-irradiated QA/QC experiments are listed in Tables 3.1-3.3, respectively. These experiments were found to be the most desirable after determining that the most appropriate photolytic technologies involved dissolved photosensitizers and solid photocatalysts as suggested by resulting publications and presentations from this project and Projects 3 and 3A (Ref. 1,2,38,53,55,56,82,85-87). During the course of this study, it became apparent that two experiments needed to be conducted as well (see Section 3- Results and Discussion and Section 6 - QA/QC Activities). These new experiments were designated 3A and 17A in Appendix A as well as in the tables below. This included the thesis work of a Metallurgical Engineering Masters graduate student who recently graduated (Ref. 82).

Iron, arsenic and manganese concentrations were measured at the start and conclusion of each photo-oxidation experiment using a Varian Liberty 110 Inductively-Coupled Plasma (ICP) spectrophotometer in accordance with EPA Method 6010A, Inductively Coupled Plasma-Atomic Emission Spectroscopy (Ref. 88). Sulfate concentrations were measured at the start and conclusion of each photo-reduction experiment using a Dionex DX-100 Model DX 1-03 ion chromatograph (IC) equipped with an IONPAC® AS4A analytical column (P/N 37041), an IONPAC® AG4A guard column (P/N 30742), and an ion self suppressor (P/N 43189). This was in accordance with EPA Method 300.0, The Determination of Inorganic Anions in Water by Ion Chromatography (Ref. 89). ICP and IC measurements were conducted outside the reaction vessel by taking appropriate sample volumes with syringe filters and diluting as necessary with appropriate matrix solutions. Plastic vials (VWR) were used for temporary storage of samples until analyses could be made. Arsenic and manganese concentration measurements were deemed as non-critical (see Section 6 - QA/QC Activities) whereas iron and sulfate concentration measurements were deemed as critical (Ref. 4). The pH conditions were measured in-situ at the start and conclusion of each test as well as at least twice during the progress of the experiments using an Orion combination pH electrode (Model 81-02) coupled to an Orion pH meter (Model 920A) in accordance with EPA Method number 4500, Electrometric Measurement (Ref. 90).

3.2 Experimental Results

In this section, the results of iron photo-oxidation and sulfate photo-reduction are further discussed to delineate the effect of UV radiation. Experiments were conducted in the absence and presence of both UV radiation and photochemicals. UV wavelengths were varied among 365 nm, 254 nm and 185 nm. Photochemicals included hydrogen peroxide and anatase for the iron photo-oxidation experiments and hydrazine hydrate, sodium formate, and anatase for the sulfate photo-reduction experiments. Results listed in Appendix A as % Fe and % SO_4^{2-} remediation were determined from the QA/QC data presented in Appendix B. Results in Appendix A are grouped into appropriate figures and tables in order to discuss the effects of certain parameters such as pH and wavelength on remediation.

3.2.1 Iron Photo-Oxidation

Fifteen experiments on iron oxidation were conducted to determine the effect a number of parameters: photochemical type and amount, wavelength, presence of UV, oxygen, and kinetics.

3.2.1.1 Anatase

Iron remediation by photo-oxidation was examined as a function of anatase addition in the presence of 254 nm UV radiation and oxygen. Results after 1.5 hours of equilibration are listed in Table 3.4. In the absence of anatase (i.e., direct photolysis), only 3.1% remediation was observed. By comparison, Table 3.4 clearly show that iron remediation can be improved using solid photocatalysis with anatase.

Unfortunately, the level of remediation is low, barely in excess of 6%. The results also indicate that there is an upper level of anatase amount to add, perhaps near 0.2 g/l, such that the addition of more anatase does not lead to more remediation. This behavior can be attributed to the design of the reactor (see Figure 3.1) which is simple in nature but does not take into account the shallow depth of UV penetration through water. To remedy this, other more appropriate designs could have been used but were too expensive to consider for this evaluation study (Ref. 91,92).

3.2.1.2 Hydrogen Peroxide

Iron removal was also examined as a function of the amount of H_2O_2 added in the presence of 254 nm UV radiation and oxygen. Results after 1.5 hours of equilibration are listed in Table 3.5 and indicate that, as the amount of H_2O_2 is increased, the amount of iron remediation is also increased. However, like the anatase, the amount of remediation increases drastically initially but higher dosages do not increase the amount of remediation significantly. In this case, increasing the dosage of H_2O_2 from 0.25 ml to 1.25 ml increases iron remediation from 28.8% to 32.2%, a mere 3.4%. Although 100% Fe remediation would have been preferred to observe, an examination of Figures 2.14 and 2.15 shows that these results concur with the preliminary investigations. According to solubility diagrams of ferrihydrite and other similar iron compounds, had higher pH values been tested, Fe remediation percentages would have been improved (see Figure 3.2).

3.2.1.3 Wavelength

Experiments were conducted on Berkeley Pitlake water to examine the effects of wavelength on iron removal using H_2O_2 and O_2 -sparging. After conducting the experiments for 1.5 hours, results show that shorter wavelengths are more efficient (see Table 3.6). Because photolysis cannot occur unless the UV radiation is absorbed, the improved performance at lower wavelengths is attributed to improved UV absorbance. UV-vis absorbance spectrum of H_2O_2 at low pH in Figure 3.3 show that strong absorbance at low wavelengths do indeed occur.

3.2.1.4 Direct Photolysis

Experiments were conducted on Berkeley Pitlake water to examine the effects of UV radiation in the absence of photochemical reagents and without O_2 -sparging. After conducting the experiments for 1.5 hours, results in Table 3.7 show that direct photolysis appears to occur but is rather slow with less than 1% Fe remediation being observed. Furthermore, the process appears to be dependent on wavelength with the longer wavelength yielding higher remediation: 254nm yielded 0.66% remediation and 185nm yielded 0.16% remediation. The results are insignificant except to illustrate that photolytic processes may be occurring naturally in the Berkeley Pitlake. This an important conclusion for future studies (Ref. 6).

3.2.1.5 Oxygen

The effect of oxygen was investigated for both the TiO_2 and H_2O_2 photolytic systems using 254 nm UV radiation. Results that were obtained after 1.5 hours of equilibrating are presented in Table 3.8. Interestingly, iron remediation is observed to decrease when O_2 is present. For TiO_2 , iron remediation decreased from 8.1% to 6.2% and, for H_2O_2 , it decreased from 31.8% to 28.8%. These differences are attributed to O_2 lowering the oxidation potentials of the valence band holes of TiO_2 and hydroxyl radicals from H_2O_2 . In other words, because the $\text{OH}^\bullet/\text{H}_2\text{O}_2$ redox couple is higher than the $\text{H}_2\text{O}_2/\text{O}_2$ redox couple, ferrous-to-ferric oxidation is more complete in the absence of oxygen. This “mixed-potential” result suggests that oxygen should not be used in these photolytic systems. It is interesting to note that the preliminary experiments conducted by Cashin and Young (Ref. 81) were conducted in this manner. Consequently, it can be concluded this is why MnO_2 precipitation was not observed in this study.

In order to examine the effect of O_2 further, experiments were conducted in the absence of UV

radiation. Results presented in Table 3.9 illustrate that the presence of O₂ is deleterious to H₂O₂ oxidation even in the absence of UV radiation. This can be attributed to the “mixed-potential” phenomenon mentioned above, thereby suggesting that oxygen should not be used in these systems either.

3.2.1.6 UV Radiation

The effect of 254nm UV radiation on Fe can be determined by comparing the results of experiments 3 and 17, 5 and 18, and 6 and 19. Experiments 3 and 17 were conducted with H₂O₂ and without O₂, Experiments 5 and 18 were conducted without H₂O₂ and with O₂ and, Experiments 7 and 19 were conducted with H₂O₂ and with O₂. In each case, Fe remediation decreases significantly upon UV irradiation. The decrease is minimal when H₂O₂ is present: 34.7% to 31.8% without O₂ and 30.6% to 28.8% with O₂; however, the decrease is significant when H₂O₂ is absent: 12.2% to 0.31%. Surprisingly, these results suggest that the use of UV radiation for the remediation of acid-mine drainage is inappropriate. In defense of this conclusion, it is important to note (1) that these results were obtained with a one-time addition of H₂O₂ at the start of the experiments as opposed to staged or continuous addition which would likely be the case in an industrial setting, and (2) that non-QA/QC data presented in Figures 2.14 and 2.15 indicate that UV radiation may prevent adsorption of some metal cations at the surface of precipitates due to photocatalytic activities.

3.2.1.7 Kinetics

In order to further understand the effect of UV, experiments 3 and 17 were reconducted as specified (i.e., in the absence of oxygen but with and without 254nm UV radiation, respectively). However, in this case, samples were taken periodically so results could be analyzed kinetically. These experiments, designated as 3A and 17A in Appendix A, were conducted according to QA/QC procedures but were determined to be important enough to include even though the QAPP did not require them (see Section 6 - QA/QC Activities). Results are presented in Figure 3.4. Results show Fe remediation was 32.8% in the absence of UV radiation and 30.2% in the presence of UV radiation. These results are quite comparable to the QA/QC results of 34.7% and 31.8% obtained for the original experiments and consequently confirm that Fe remediation with H₂O₂ is best in the absence of UV. However, it is critical to note that the reaction profiles in Figure 3.4 clearly show that H₂O₂ photolysis is the better process in the first ten minutes; and this reaction profile would likely have progressed had the H₂O₂ been added continuously or in stages as opposed to only at the start of the test.

In lieu of these comments, the data was replotted using time as a logarithmic scale (see Figure 3.5). The resulting profile for the non-irradiated sample shows at least one plateau indicating that there is an initial slow reaction which must first be overcome before Fe oxidation actually occurs. This behavior can be attributed to the oxidation of another species, most likely organic in nature. The lack of plateaus for the irradiated sample suggests the reaction of hydroxyl radicals with the suspected organic is significantly faster due to resulting higher oxidation potentials and therefore a stronger driving force to react. At pH 7, the H₂O₂/H₂O couple has a reversible potential near 1.3 volts vs SHE and the OH^{*}/H₂O couple is near 2.1 volts vs. SHE (Ref. 18-20,60,93). Consequently, under non-irradiated conditions, H₂O₂ has a longer lifetime (which explains why pharmaceutical H₂O₂ is stored in brown bottles) and is more efficient at reacting on a molar basis. It can thus be concluded that, under irradiated conditions, H₂O₂ should be added continuously or, at least, in stages to overcome this

problem and, in this regard, UV irradiation would likely prove to be better than non-irradiated systems. Clearly, though, more research is needed.

3.2.2 Sulfate Photo-Reduction

Seven experiments on sulfate reduction were conducted to see if sulfide could be produced using several photochemicals either individually or in combination and in the absence or presence of 254nm UV radiation. Argon gas was continually sparged to help remove dissolved oxygen and thereby maximize reducing conditions.

3.2.2.1 Photochemicals

Sulfate photo-reduction experiments were conducted with Na-formate, hydrazine, and anatase. Because the literature concludes that a combination of dissolved photochemicals works better in the presence of a solid photocatalyst (Ref. 22-25), experiments were also conducted using formate/anatase and hydrazine/anatase combinations. Results presented in Table 3.11 show the best remediation of 9.2% was obtained with hydrazine alone followed by 6.7% remediation with formate alone. When anatase was used in combination with hydrazine and formate, sulfate remediation worsened to 5.4% and 2.9%, respectively. These results clearly show that, in the case of remediating acid-mine waters, the combination of photochemicals is detrimental. This has been observed previously for hydrogen peroxide/anatase and was attributed to the formation of a titanium complex (Ref. 59,86). Such a conclusion could be reached here but would be speculation at best. Finally, results obtained with anatase alone was the worst at 2.3% sulfate remediation.

3.2.2.2 UV Radiation

In order to insure that sulfate photoreduction is fact, Experiments 12 and 13 were repeated in the absence of UV radiation and designated as Experiments 20 and 21. The results of these four experiments are listed in Table 3.12. Unlike Fe photo-oxidation results, Table 3.12 indicates that sulfate remediation is best in the presence of UV. Due to the redox nature of the photochemicals tested, it can also be concluded that sulfate photo-reduction improves with increased reducing power and that power improves upon UV irradiation. E_H measurements conducted simultaneously to the process showed that the potentials were not low enough to reduce the sulfate to the desired sulfide (see Figure 2.7).

In general, it is intriguing that sulfate concentrations were observed to decrease in all of these experiments. Unfortunately, sulfide formation was never observed and, as a result, sulfide precipitation for selective recovery of copper, zinc and cadmium could not be tested. It can therefore be concluded that further research is needed to find a way to achieve this photolytic goal.

3.3 Summary

Photo-oxidation experiments of Berkeley Pitlake water were conducted to remediate ferrous (Fe^{2+}), manganous (Mn^{2+}) and arsenate (AsO_4^{3-}) ions with anatase (titanium dioxide, TiO_2) and hydrogen peroxide (H_2O_2). Ferrous and manganous ions were expected to be removed by their oxidation to ferric and manganese(IV) and subsequent precipitation as ferrihydrite and pyrolusite, respectively. On the other hand, arsenate remediation was expected to occur via adsorption at the surface of the precipitated ferrihydrite. In addition, photo-reduction experiments for sulfate remediation were conducted using strong reducing agents of sodium formate ($NaCOOH$) and hydrazine (H_4N_2) in the

absence and presence of the anatase (TiO_2) in hopes of producing sulfide (S^{2-}) for the additional remediation of additional mobile toxic constituents such as cupric (Cu^{2+}), zincic (Zn^{2+}), and cadmous (Cd^{2+}) cations via their precipitation as sulfide compounds. Reaction efficiencies were calculated and compared as remediation percentages for all experiments.

Results showed that sulfate photo-reduction worked but, under the conditions examined, was not 100% effective. Photo-reduction the dissolved photochemicals proved to work best with hydrazine and formate yielding 9.2% and 6.7% remediation, respectively. When hydrazine and formate were used simultaneously with anatase, remediation percentages decreased to 5.4% and 2.9%, respectively. Anatase, by itself, only yielded 2.3% remediation. Consequently, it is concluded that the presence of anatase, as a solid photocatalyst, with either hydrazine or formate, as dissolved photochemicals, is detrimental to the homogeneous photolysis processes. Although sulfide formation was never observed, it is clear that photo-reduction of sulfate is possible with both homogeneous photolysis and heterogeneous photocatalysis.

By comparison, ferrous photo-oxidation could be 100% effective but was found to be dependent on the conditions applied, especially pH. Results indicated that homogeneous photolysis with hydrogen peroxide worked better than heterogeneous photocatalysis with anatase yielding 28.8% remediation versus 6.1% remediation. Higher dosages of either photochemical yielded only marginal improvement in remediation. Further experiments showed that photolysis with hydrogen peroxide improved with decreasing wavelegth, but was actually best in the absence of UV radiation. This surprising result was attributed to bubbling in oxygen during the experiments as well as to not adding the photochemical continuously and observing a side reaction for only the UV-assisted experiments. The side reaction was further attributed to photo-oxidation of organic species. Oxygen bubbling was believed to have created a mixed potential which lowered the solution potential (E_H) in the experiments below the potential required for manganous oxidation to occur. In this regard, manganous concentrations were not observed to change and its measurement was therefore removed from the critical list.

Unfortunately, the selected pH condition of 3 was too low to observe adequate ferrous remediation. Iron concentrations in solution therefore remained high and interfered with the arsenic concentration measurement by ICP. In this regard, arsenic concentrations were unable to be determined and its measurement was also removed from the critical list.

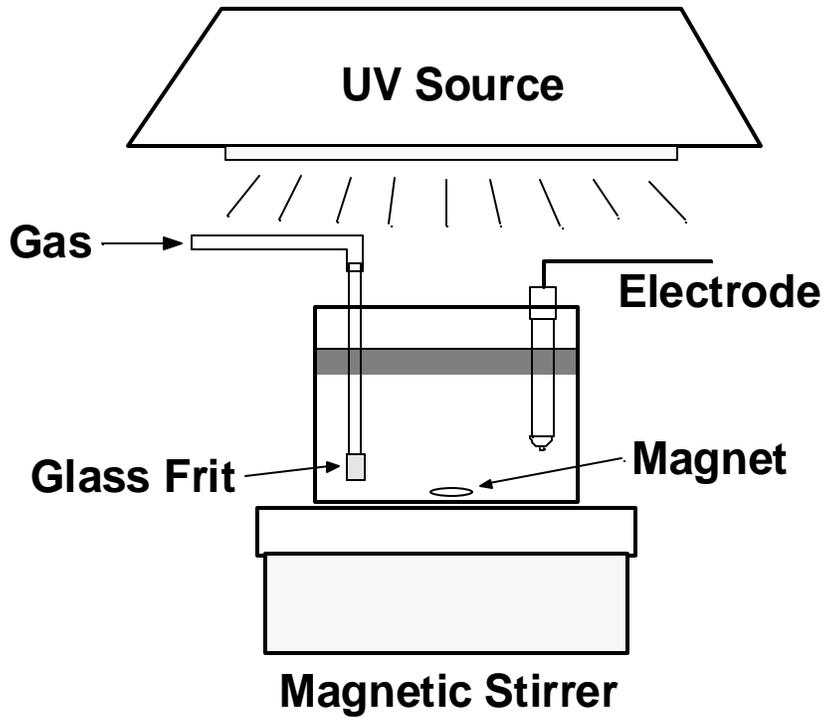


Figure 3.1. Experimental setup for QA/QC work in MWTP Activity IV, Project 3B.

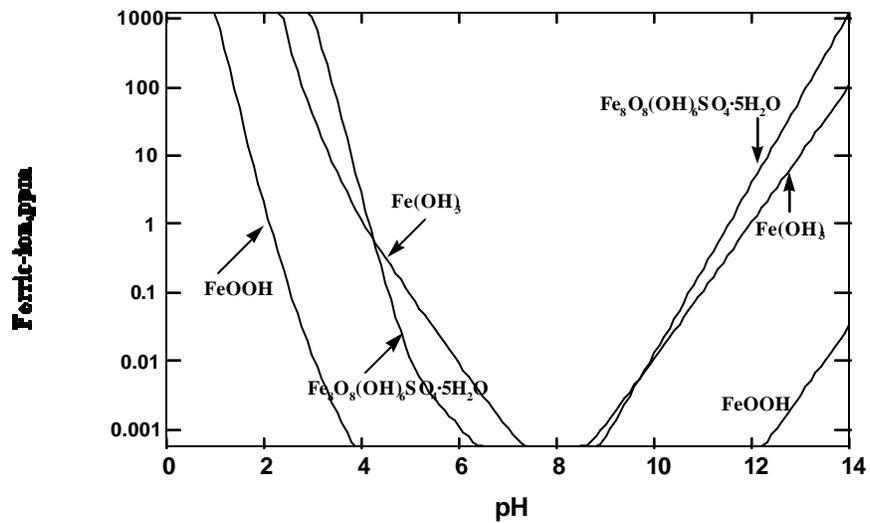


Figure 3.2. Solubilities of ferrihydrite, $\text{Fe}(\text{OH})_3$; schwertmannite, $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \cdot 5\text{H}_2\text{O}$; and goethite, FeOOH in concentration of iron (III) as a function of pH.

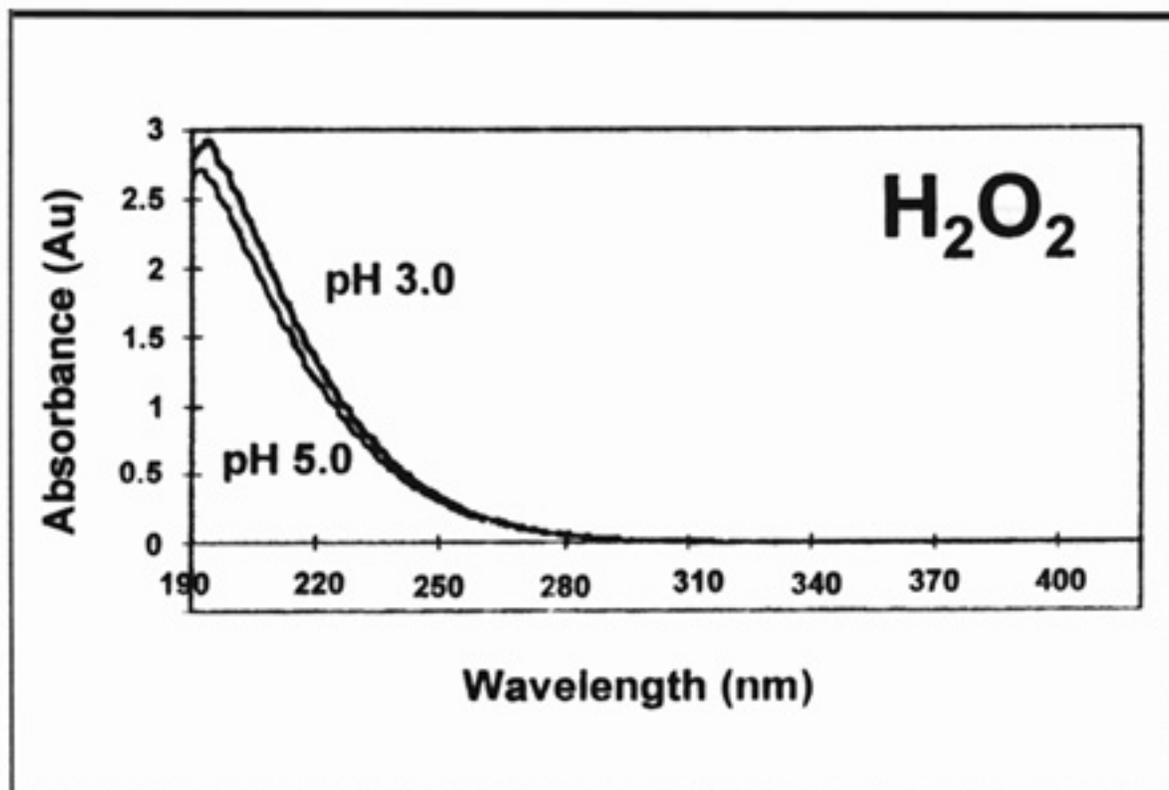


Figure 3.3. UV-vis absorbance spectra of hydrogen peroxide at pH 3 and 5.

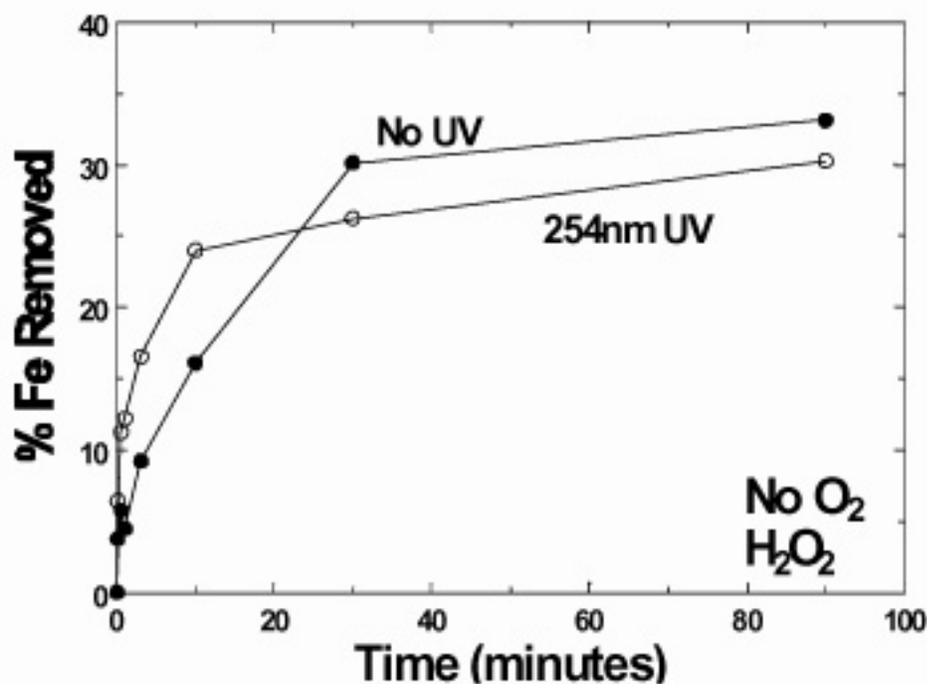


Figure 3.4. Plot to compare the Fe remediation kinetics of UV irradiated and non-irradiated samples of Berkeley Pitlake water with H_2O_2 in the absence of O_2 .

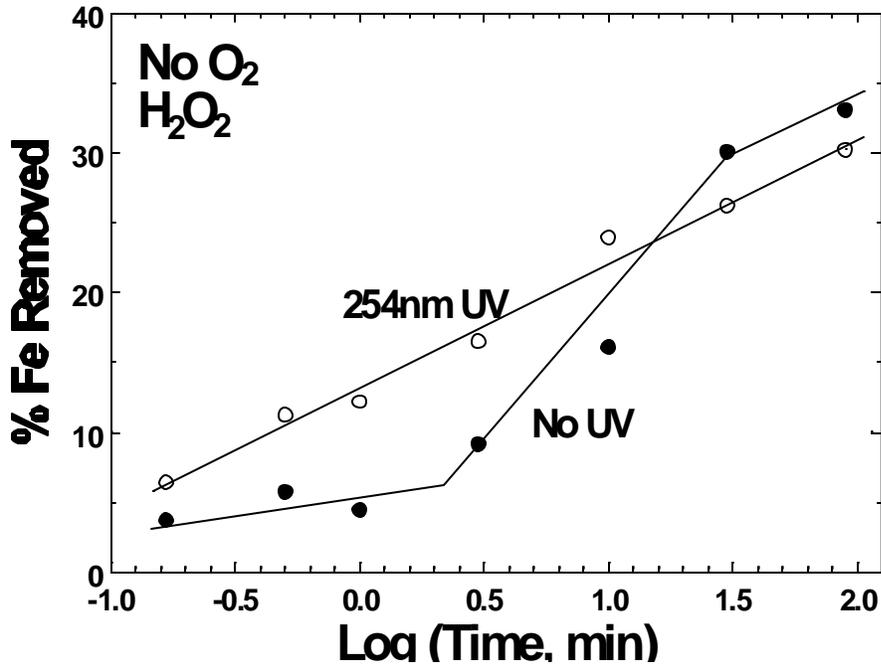


Figure 3.5. Semi-logarithmic plot to compare the Fe remediation kinetics of UV irradiated and non-irradiated samples of Berkeley Pitlake water with H₂O₂ in the absence of O₂.

Table 3.1 Photo-oxidation Test Conditions and Reagent Schedules for Project 3B.

Experiment No.	UV Wavelength	Photolytic Reagent Concentration or Amount	Sparging Gas
1	185nm	None	None
2	254nm	None	None
3	254nm	30% H ₂ O ₂ (0.25 ml)	None
3A	254nm	30% H ₂ O ₂ (0.25 ml)	None
4	254nm	TiO ₂ (2.0 g/l)	None
5	254nm	None	O ₂
6	185nm	30% H ₂ O ₂ (0.25 ml)	O ₂
7	254nm	30% H ₂ O ₂ (0.25 ml)	O ₂
8	254nm	30% H ₂ O ₂ (1.25 ml)	O ₂
9	365nm	30% H ₂ O ₂ (0.25 ml)	O ₂
10	254nm	TiO ₂ (0.2 g/l)	O ₂
11	254nm	TiO ₂ (2.0 g/l)	O ₂

Table 3.2. Photo-reduction Test Conditions and Reagent Schedules for Project 3B.

Experiment No.	UV Wavelength	Photolytic Reagent Concentration or Amount	Sparging Gas
12	254nm	Na-Formate (0.5 M)	Ar
13	254nm	Hydrazine (0.5 M)	Ar
14	254nm	TiO ₂ (2.0 g/l)	Ar
15	254nm	TiO ₂ (2.0 g/l) Na-Formate (0.5 M)	Ar
16	254nm	TiO ₂ (2.0 g/l) Hydrazine (0.5 M)	Ar

Table 3.3. Non-Irradiated Test Conditions and Reagent Schedules for Project 3B.

Experiment No.	Sample Test	Photolytic Reagent Concentration or Amount	Sparging Gas
17	Oxidation	30% H ₂ O ₂ (0.25 ml)	None
17A	Oxidation	30% H ₂ O ₂ (0.25 ml)	None
18	Oxidation	None	O ₂
19	Oxidation	30% H ₂ O ₂ (0.25 ml)	O ₂
20	Reduction	Na-Formate (0.5 M)	Ar
21	Reduction	Hydrazine (0.5 M)	Ar

Table 3.4. Effect of Anatase on Iron Remediation using 254 nm UV radiation and O₂.

Experiment No.	TiO ₂ Amount	% Fe Remediation
5	0 g/l	0.31
10	0.2 g/l	6.10
11	2.0 g/l	6.24

Table 3.5. Effect of H₂O₂ on Iron Remediation using 254 nm UV radiation and O₂.

Experiment No.	H ₂ O ₂ Amount	% Fe Remediation
5	0 ml	0.31
7	0.25 ml	28.8
8	1.25 ml	32.2

Table 3.6. Effect of UV wavelength on Iron Remediation using 0.25 ml H₂O₂ and O₂.

Experiment No.	UV Wavelength	% Fe Remediation
6	185 nm	32.0
7	254 nm	28.8
9	365 nm	23.0

Table 3.7. Effect of UV Wavelength on Iron Remediation without Chemical Addition.

Experiment No.	UV Wavelength	% Fe Remediation
1	185 nm	0.16
2	254 nm	0.66

Table 3.8. Effect of O₂ on Iron Remediation using 254nm UV radiation and H₂O₂ or TiO₂.

Experiment No.	Reagent	Condition	% Fe Remediation
3	H ₂ O ₂	No O ₂	31.8
7	H ₂ O ₂	O ₂	28.8
4	TiO ₂	No O ₂	8.05
10	TiO ₂	O ₂	6.10

Table 3.9. Effect of O₂ on Iron Remediation using H₂O₂ in the Absence of UV Radiation.

Experiment No.	Condition	% Fe Remediation
17	No O ₂	34.7
19	O ₂	30.6

Table 3.10. Effect of 254nm UV on Iron Remediation under Different Conditions.

Experiment No.	Conditions		% Fe Remediation
3	H ₂ O ₂ no O ₂	UV	31.8
17		no UV	34.7
5	no H ₂ O ₂ O ₂	UV	0.31
18		no UV	12.2
7	H ₂ O ₂ O ₂	UV	28.8
19		no UV	30.6

Table 3.11. Effect of Different Photochemicals on SO₄²⁻ Remediation with Ar-Sparging.

Experiment No.	Conditions	% SO ₄ ²⁻ Remediation
12	0.5 M Formate	6.7
13	0.5 M Hydrazine	9.2
14	2 g/l Anatase	2.3
15	0.5 M Formate 2 g/l Anatase	2.9
16	0.5 M Hydrazine 2 g/l Anatase	5.4

Table 3.12. Effect of 254nm UV on SO_4^{2-} Remediation with Ar-Sparging.

Experiment No.	Conditions		% SO_4^{2-} Remediation
12	Formate	UV	6.7
20		no UV	0.34
13	Hydrazine	UV	9.2
21		no UV	0.52

4. QUALITY ASSURANCE/QUALITY CONTROL

The major purposes of this MWTP project were identifying photolytic processes that could be used for the remediation of acid mine drainage waters and evaluating the processes to assess their scientific feasibility via determining reaction efficiencies so that recommendations could be made to continue this research effort. The programmatic and regulatory setting in which the project quality assurance was conducted was Category IV as outlined in MWTP Activity IV, Project 3B QAPP (Ref. 4). Projects are designated Category IV when they are used to produce results for the purpose of assessing suppositions. Existing background data presented in Section 2 - Photochemistry was not required to conform to any criteria. This information is considered common knowledge since it was predominantly the foundation to the workplan (Ref. 3).

4.1 QA/QC Objectives

The Quality Assurance/Quality Control (QA/QC) objectives outlined for the project were specified to generate acceptable data. The MWTP Activity IV, Project 3B QAPP (Ref. 4) was provided to insure:

- C measurements were appropriate for achieving project objectives,
- C quality control procedures were sufficient for obtaining data of known and adequate quality, and
- C such data would be defensible if technically challenged.

Ultimately, it would be desirable to show that the selected photolytic technologies for the remediation of acid mine drainage waters yielded concentrations below the U.S. EPA Drinking Water Standards. However, as noted in Section 2.3 - Experimental Results, pH control was conducted at too low of a pH for adequate precipitation of the iron thereby causing interference problems for the detection and quantification of arsenic concentrations (see Section 6 - QA/QC activities). Furthermore, the use of oxygen gas appeared to cause a mixed potential to develop which prevented the high redox potential of hydroxyl radicals from being reached. This was used to explain why manganese remediation was not observed in this investigation as opposed to a preliminary study (see Ref. 81 and Section 6 - QA/QC Activities). Nevertheless, project objectives were to identify and then evaluate appropriate photolytic processes that remediate the wastewater, not necessarily achieve the Drinking Water Standard. This task would be reserved for future studies and accordingly recommended if such concentrations were obtained.

4.2 Analyses

Berkely Pitlake test solutions were monitored for iron, manganese, arsenic and sulfate concentrations as well as for pH conditions. Only U.S. EPA-approved methods were employed.

4.2.1 Procedures

U.S. EPA-approved methods (Ref. 88-90) included Electrometric Measurement (Method No. 4500) pH, Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0) for sulfate concentration measurements, and inductively coupled plasma spectroscopy (Method No. 6010A) for iron, manganese and arsenic concentration measurements. Electrometric measurements for pH were conducted in the reaction vessel every hour. The pH was controlled at pH 3 for photo-oxidation experiments using drops from NaOH or H₂SO₄ solutions, as needed. However, for photo-reduction experiments, the pH was controlled at pH 6 using drops from NaOH or HNO₃ solutions, as needed. Sulfate concentrations were determined by first diluting a sample with a matrix of

deionized/distilled water (usually 1:20) and then taking and injecting a 1-ml aliquot sample into the ion chromatograph. Because the photoreduction experiments were conducted at pH 6, the deionized/distilled water had no effect on the sample. Samples may have been stored temporarily in 20 ml plastic vials between measurements. Equipment manufacturers and types are specified in Section 3 - Treatability.

4.2.2 Calibrations

pH meter. For photo-oxidation experiments, buffer solutions at pH 1.0 and 4.0 were used in the standard two-point calibration of the pH meter. For photo-reduction experiments, buffer solutions at pH 4.0 and 7.0 were used. The buffer pH values bracketed the pH control that was required. The pH meter was recalibrated after every 20 measurements and at the conclusion of every test. Percent slopes were consistently found to be $100\% \pm 5\%$. Measurements of pH were non-critical to all tests.

Ion chromatograph. Before every photo-reduction test, a blank and sulfate standards were used to establish working curves between 0 and 1000 ppm. This calibration range bracketed all sulfate concentrations measured but required aliquots to be diluted by at least a factor of 10; normally, a dilution ratio of 1:20 was used. Calibration curves were analyzed by PeakSimple data software (SRI Instruments) using R^2 -correlation coefficients. In this regard, R^2 -values typically measured 0.97 which was consistently greater than the 0.90 acceptance criterium. Although never encountered, the ion chromatograph was to be recalibrated if a standard, upon being checked after every 20 measurements, was outside 75-125% linear range. Sulfate measurements were critical to all photo-reduction tests but were non-critical to the photo-oxidation tests.

ICP Spectrophotometer. Before every photo-oxidation test, arsenic, manganese and iron standards of 0.1, 1.0, 10 and 50 ppm were used to establish working curves. This calibration range bracketed all concentrations measured but required samples to be diluted with a 5% HNO_3 matrix by a typical factor of 10 depending on which element was being analyzed. Instrument detection limits (IDL) were determined to be 0.052, 0.162 and 0.003 ppm for As, Fe and Mn, respectively. This met acceptable criteria. These concentration measurements were critical to all photo-oxidation tests.

5. FIELD SAMPLES

Berkeley Pitlake water measuring 5 gallons was collected and transported to the ELC Building at Montana Tech by the Montana Bureau of Mines and Geology. The water was obtained from the 200-foot depth (i.e., deep Berkeley Pitlake water) and stored in a refrigerator to help maintain freshness throughout the duration of the QA/QC work. Aliquats measuring 150 milliliters (ml) were taken from this sample for each of the 21 experiments. All experiments were conducted with reagent grade chemicals named earlier with the industrial supplier (see Section 3 - Treatability).

6. QA/QC CHECK PROCEDURES AND ACTIVITIES

6.1 Check Procedures

Numerous procedures were in place to assure that quality data was reported. These check procedures included

- C recalibrating the various instruments used through the course of the tests as described in Section 4 - Quality Assurance/Quality Control,
- C analyzing calibration standards periodically to assure the various instruments were functioning properly as also described in Section 4 - Quality Assurance/Quality Control,
- C measuring reagent blanks periodically to make sure the various instruments were not contaminated thereby giving false readings,
- C running a duplicate sample to assure the data was reproducible,
- C running a second duplicate sample in the dark to verify effects of UV radiation,
- C matrix-spiking a test to assure the various instruments were functioning properly thereby yielding results within 75-125% recovery,
- C using laboratory fortified blanks for determining acceptable performance of the ion chromatograph,
- C establishing proficiency on the ion chromatograph by measuring 4 equally prepared aliquots, calculating average % recoveries, standard deviations, and upper and lower control limits, and by comparing results to values found in the accuracy and precision table found in Determination of Inorganic Anions in Water by Ion Chromatography (Method No. 300.0), and
- C verifying inter-element interference and background correction factors for the ICP.

Only two of these QA/QC check procedures were found to fail. Corrective actions were taken and are described in the ensuing section.

6.2 Activities

During the course of the QA/QC experiments, only two problems were observed which required QA/QC activities. These activities involved ICP procedures:

- C Early on, photo-oxidation experiments were conducted and all QA/QC criteria would pass except one; recovery calculations following the analysis of matrix spike solutions would be <20%. Because acceptable criteria is 75-125%, a matrix effect was suspected. It was found that 2% HNO₃ standards were being used while samples were being prepared with 5% HNO₃. Standards at the higher acid concentration were then obtained and the problem was remedied, and
- C Throughout, photo-oxidation experiments showed arsenic concentrations to be zero at the start and finish. Inter-element interference with iron was suspected due to the high concentration of iron in the initial and final solutions. Because this problem could not be overcome, a request was written to and accepted by EPA to remove arsenic from the critical measurement list. Nevertheless, arsenic concentrations were non-critically measured through the all of the QA/QC work. At the same time, a request to EPA was made and accepted to also remove manganese from the critical measurement list. This activity was needed because manganese concentrations, unlike in the preliminary studies, was not being remediated and goals were thus not being obtained. Reason for this behavior was attributed to oxygen (i.e., samples were bubbled with oxygen) causing a lower-than-desired potential to develop between oxygen and water. Presumably, hydroxyl radicals, with water and in the absence of oxygen, should

produce a higher potential and cause manganous cations to oxidize and precipitate as pyrolusite.

In addition to solving these two problems, QA/QC activities were taken to develop a better understanding of what happens when photochemical reactions are induced in Berkeley Pitlake water, especially since early conclusions were being drawn that suggested not to use photolysis for its remediation. In this regard, it became apparent that two experiments needed to be conducted, one in the absence and the other in the presence of UV radiation, for kinetic analysis. These two experiments were conducted using QA/QC protocol but are not listed in the QAPP (Ref. 4). Appendix A and various tables in Section 3 show these experiments to be Experiments 3A and 17A.

7. CONCLUSIONS

7.1 Summary

Photo-oxidation experiments of Berkeley Pitlake water were conducted to remediate ferrous (Fe^{2+}), manganous (Mn^{2+}) and arsenate (AsO_4^{3-}) ions with anatase (titanium dioxide, TiO_2) and hydrogen peroxide (H_2O_2). Ferrous and manganous ions were expected to be removed by their oxidation to ferric and manganese(IV) and subsequent precipitation as ferrihydrite and pyrolusite, respectively. On the other hand, arsenate remediation was expected to occur via adsorption at the surface of the precipitated ferrihydrite. In addition, photo-reduction experiments for sulfate remediation were conducted using strong reducing agents of sodium formate (NaCOOH) and hydrazine (H_4N_2) in the absence and presence of the anatase (TiO_2) in hopes of producing sulfide (S^{2-}) for the additional remediation of additional mobile toxic constituents such cupric (Cu^{2+}), zincic (Zn^{2+}), and cadmous (Cd^{2+}) cations via their precipitation as sulfide compounds. Reaction efficiencies were calculated and compared as remediation percentages for all experiments.

Results showed that sulfate photo-reduction worked but, under the conditions examined, was not 100% effective. Photo-reduction the dissolved photochemicals proved to work best with hydrazine and formate yielding 9.2% and 6.7% remediation, respectively. When hydrazine and formate were used simultaneously with anatase, remediation percentages decreased to 5.4% and 2.9%, respectively. Anatase, by itself, only yielded 2.3% remediation. Consequently, it is concluded that the presence of anatase, as a solid photocatalyst, with either hydrazine or formate, as dissolved photochemicals, is detrimental to the homogeneous photolysis processes. Although sulfide formation was never observed, it is clear that photo-reduction of sulfate is possible with both homogeneous photolysis and heterogeneous photocatalysis.

By comparison, ferrous photo-oxidation could be 100% effective but was found to be dependent on the conditions applied, especially pH. Results indicated that homogeneous photolysis with hydrogen peroxide worked better than heterogeneous photocatalysis with anatase yielding 28.8% remediation versus 6.1% remediation. Higher dosages of either photochemical yielded only marginal improvement in remediation. Further experiments showed that photolysis with hydrogen peroxide improved with decreasing wavelegth, but was actually best in the absence of UV radiation. This surprising result was attributed to bubbling in oxygen during the experiments as well as to not adding the photochemical continuously and observing a side reaction for only the UV-assisted experiments. The side reaction was further attributed to photo-oxidation of organic species. Oxygen bubbling was believed to have created a mixed potential which lowered the solution potential (E_H) in the experiments below the potential required for manganous oxidation to occur. In this regard, manganous concentrations were not observed to change and its measurement was therefore removed from the critical list. Unfortunately, the selected pH condition of 3 was too low to observe adequate ferrous remediation. Iron concentrations in solution therefore remained high and interfered with the arsenic concentration measurement by ICP. In this regard, arsenic concentrations were unable to be determined and its measurement was also removed from the critical list.

7.2 Recommendations

Sulfate photo-reduction was shown to occur but only yielded a maximum of approximately 10% remediation. Ferrous photo-oxidation was also shown to occur but, due to the low pH conditions

studied, yielded no better than 35% remediation. Clearly, both of these processes are promising but require further investigation to improve upon reaction efficiencies as well as rates.

The sulfate photo-reduction process is appealing because it represents an opportunity to produce sulfide and thereby induce the remediation of numerous heavy metal cations via their precipitation as sulfide compounds. On the other hand, the ferrous photo-oxidation process is appealing because it can simultaneously remediate manganous and arsenate species. The remediation of manganese via this technique would establish a process where the pH does not have to be adjusted to pH 11 as required by the two-stage lime addition process which, at this time, is the best-determined available technology (BDAT) for remediating Berkeley Pitlake water (Ref. 7). In this regard, this technique could eliminate the second stage and yield substantial savings of lime.

This would require determining the effect of, for examples, pH, oxygen, continuous photochemical addition, and wavelength on the two processes. Different research areas would also include examining other solid photocatalysts, dissolved photosensitizers, other mine waste waters, concentrations of mobile toxic constituents, sparging gases, temperatures, and UV intensities. ZnO, WO₃, CdS, SiC, Fe₂O₃, and certain zeolites, for examples, would be great photocatalysts to study. Humic acid and oxalate could be interesting photosensitizers for examining. CH₄, CO, H₂, O₃, and CO₂ are excellent candidates for changing atmospheric conditions. Temperatures ranging from near-freezing to near-boiling should be examined to mimic changing conditions observed in cold and hot climates. Finally, UV intensities could be adjusted, for example, from the 600 FW/cm² used in previous studies (Ref. 1,2) to the 16,000 FW/cm² used in this study. Other intensities (and wavelengths) could be obtained from a variety of different sources including lamps, arcs and lasers. All of these options should be examined and are therefore recommended for further studies.

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Appendix A

Remediation Percentages

Table A.1 % Fe Remediation Determined by Photo-Oxidation Experiments.

Experiment No.	UV Wavelength	Photolytic Reagent Concentration or Amount	Sparging Gas	% Fe Remediation
1	185nm	None	None	0.16
2	254nm	None	None	0.66
3	254nm	30% H ₂ O ₂ (0.25 ml)	None	31.8
3A	254nm	30% H ₂ O ₂ (0.25 ml)	None	30.2
4	254nm	TiO ₂ (2.0 g/l)	None	8.05
5	254nm	None	O ₂	0.31
6	185nm	30% H ₂ O ₂ (0.25 ml)	O ₂	32.0
7	254nm	30% H ₂ O ₂ (0.25 ml)	O ₂	28.8
8	254nm	30% H ₂ O ₂ (1.25 ml)	O ₂	32.2
9	365nm	30% H ₂ O ₂ (0.25 ml)	O ₂	23.0
10	254nm	TiO ₂ (0.2 g/l)	O ₂	6.10
11	254nm	TiO ₂ (2.0 g/l)	O ₂	6.24
17	None	30% H ₂ O ₂ (0.25 ml)	None	34.7
17A	None	30% H ₂ O ₂ (0.25 ml)	None	32.8
18	None	None	O ₂	12.2
19	None	30% H ₂ O ₂ (0.25 ml)	O ₂	30.6

Table A.2 % SO₄²⁻ Remediation Determined by Photo-Reduction Experiments.

Experiment No.	UV Wavelength	Photolytic Reagent Concentration or Amount	Sparging Gas	% SO₄²⁻ Remediation
12	254nm	Na-Formate (0.5 M)	Ar	6.7
13	254nm	Hydrazine (0.5 M)	Ar	9.2
14	254nm	TiO ₂ (2.0 g/l)	Ar	2.3
15	254nm	TiO ₂ (2.0 g/l) Na-Formate (0.5 M)	Ar	2.9
16	254 nm	TiO ₂ (2.0 g/l) Hydrazine (0.5 M)	Ar	5.4
20	None	Na-Formate (0.5 M)	Ar	0.34
21	None	Hydrazine (0.5 M)	Ar	0.52

Appendix B

QA/QC Data

QC Procedures

Section 7.1.1. Analyze calibration standard (ICV) Acceptable Criteria	measured conc. true value	10%				Section 8.5.2. Matrix spikes Recovery			
As	1.039	1.004	ppm	3.49	%	As	Unspike (U) B.D.L.	Spike (S) B.D.L.	Actual conc. R %
Al	18.87	20.955	ppm	-5.91	%	Al	0.08282	0.06538	0.0194
Mn	1.604	1.503	ppm	6.72	%	Mn	0.05184	0.07215	0.086
Fe	9.576	9.995	ppm	4.19	%	Fe	0.2076	0.2735	104
Mg	505.2	500.828	ppm	0.87	%	Mg	B.D.L.	B.D.L.	77
Ca	496.5	500.002	ppm	-0.70	%	Ca	B.D.L.	B.D.L.	
Section 8.3. Method blank Acceptable Criteria						Section 8.4. Analytical duplicates RPD			
		N/A							$RPD = 100 * (C1-C2)/(C1+C2)/2$
As	measured conc. B.D.L.	C.R.D.L. 0.01	ppm			As	C1 B.D.L.	C2 B.D.L.	RPD %
Al	0.09011	0.20	ppm			Al	0.08282	0.05605	0.48
Mn	B.D.L.	0.015	ppm			Mn	0.05184	0.05159	0.73
Fe	0.03981	0.10	ppm			Fe	0.2076	0.2061	
Mg	B.D.L.	5.00	ppm			Mg	B.D.L.	B.D.L.	
Ca	B.D.L.	5.00	ppm			Ca	B.D.L.	B.D.L.	
Section 8.6.1.1. Check standard Acceptable Criteria						Section 8.6.1.2. Calibration blank (CCB) Acceptable Criteria			
		10%							
As	measured conc. 0.4996	true value 0.502	ppm	-0.48	%	As	measured co B.D.L.	C.R.D.L. 0.01	ppm
Al	9.526	10.03	ppm	-5.01	%	Al	B.D.L.	0.20	ppm
Mn	0.749	0.752	ppm	0.40	%	Mn	B.D.L.	0.015	ppm
Fe	4.785	5.00	ppm	-4.26	%	Fe	B.D.L.	0.10	ppm
Mg	233.7	250.41	ppm	-6.67	%	Mg	B.D.L.	5.00	ppm
Ca	235.5	250.00	ppm	5.80	%	Ca	B.D.L.	5.00	ppm

Calibration of instrument

Results exported from Varian LIBERTY										
Client File		TAQAQC214								
Output Format		.DIF								
Match Sample Label										
Match Program										
Match Elements										
Date and Time		YES								
Report Mode		ALL DATA								
Report Mode = ALL DATA, Date and Time = YES										
Rack#	Tube#	Sampl.Lab.	El.	WT.	Intera	Conc.	Dilute Cor.	Units	Date	Time
1	1	1 BLANK	As	193.696	20.52	0		ppm	2/14/97	11:42:39
1	1	1 BLANK	Al	396.152	14980	0		ppm	2/14/97	11:44:27
1	1	1 BLANK	Mn	257.61	1779	0		ppm	2/14/97	11:44:51
1	1	1 BLANK	Fe	259.94	1566	0		ppm	2/14/97	11:45:17
1	1	1 BLANK	Mg	279.079	206.5	0		ppm	2/14/97	11:45:53
1	1	1 BLANK	Ca	317.933	3745	0		ppm	2/14/97	11:45:52
1	2	2 STANDARD 1	As	193.696	30	0.1		ppm	2/14/97	11:47:17
1	2	2 STANDARD 1	Al	396.152	43120	2		ppm	2/14/97	11:48:20
1	2	2 STANDARD 1	Mn	257.61	13250	0.15		ppm	2/14/97	11:48:56
1	2	2 STANDARD 1	Fe	259.94	19010	1.011		ppm	2/14/97	11:49:07
1	2	2 STANDARD 1	Mg	279.079	46450	49.95		ppm	2/14/97	11:49:27
1	2	2 STANDARD 1	Ca	317.933	560230	49.97		ppm	2/14/97	11:49:46
1	3	3 STANDARD 2	As	193.696	177.7	3.5		ppm	2/14/97	11:51:11
1	3	3 STANDARD 2	Al	396.152	144476	5.999		ppm	2/14/97	11:52:44
1	3	3 STANDARD 2	Mn	257.61	17770	0.7495		ppm	2/14/97	11:53:38
1	3	3 STANDARD 2	Fe	259.94	23010	5.05		ppm	2/14/97	11:53:51
1	3	3 STANDARD 2	Mg	279.079	472300	249.8		ppm	2/14/97	11:55:21
1	3	3 STANDARD 2	Ca	317.933	2368000	249.9		ppm	2/14/97	11:57:41
1	4	4 STANDARD 3	As	193.696	308.6	1		ppm	2/14/97	11:58:25
1	4	4 STANDARD 3	Al	396.152	255100	20		ppm	2/14/97	11:59:08
1	4	4 STANDARD 3	Mn	257.61	186400	1.459		ppm	2/14/97	11:59:52
1	4	4 STANDARD 3	Fe	259.94	154100	10.11		ppm	2/14/97	12:00:37
1	4	4 STANDARD 3	Mg	279.079	427800	99.5		ppm	2/14/97	12:01:11
1	4	4 STANDARD 3	Ca	317.933	4892000	99.7		ppm	2/14/97	12:01:56
1	5	5 STANDARD 4	Al	396.152	5276000	501.7		ppm	2/14/97	12:02:19
1	5	5 STANDARD 4	Fe	259.94	3033000	199.8		ppm	2/14/97	12:02:51
1	6	6 STANDARD 5	As	193.696	14970	50		ppm	2/14/97	12:03:40
1	6	6 STANDARD 5	Al	396.152	346.5	1.059		ppm	2/14/97	12:03:59
1	7	7 ICV	As	193.696	278700	18.87		ppm	2/14/97	12:04:35
1	7	7 ICV	Al	396.152	123400	6604		ppm	2/14/97	12:04:57
1	7	7 ICV	Mn	257.61	123400	6604		ppm	2/14/97	12:05:20
1	7	7 ICV	Fe	259.94	159600	9.376		ppm	2/14/97	12:05:39
1	7	7 ICV	Mg	279.079	467300	55.2		ppm	2/14/97	12:05:59
1	7	7 ICV	Ca	317.933	5005000	456.5		ppm	2/14/97	12:06:29
1	1	1 ICB	As	193.696	10.39	B.D.L.		ppm	2/14/97	12:07:11
1	1	1 ICB	Al	396.152	13230	B.D.L.		ppm	2/14/97	12:08:26
1	1	1 ICB	Mn	257.61	1271	B.D.L.		ppm	2/14/97	12:08:59
1	1	1 ICB	Fe	259.94	1670	B.D.L.		ppm	2/14/97	12:09:13
1	1	1 ICB	Mg	279.079	1611	B.D.L.		ppm	2/14/97	12:09:32
1	1	1 ICB	Ca	317.933	3189	B.D.L.		ppm	2/14/97	12:09:51
1	8	8 CRH	As	193.696	30.26	0.04534		ppm	2/14/97	12:11:37
1	8	8 CRH	Al	396.152	14920	B.D.L.		ppm	2/14/97	12:12:19
1	8	8 CRH	Mn	257.61	1737	0.03549		ppm	2/14/97	12:12:44
1	8	8 CRH	Fe	259.94	1645	B.D.L.		ppm	2/14/97	12:13:06
1	8	8 CRH	Mg	279.079	504.6	B.D.L.		ppm	2/14/97	12:13:26
1	8	8 CRH	Ca	317.933	3766	B.D.L.		ppm	2/14/97	12:13:45
1	5	5 ICSA1	As	193.696	4.038	B.D.L.		ppm	2/14/97	12:15:31
1	5	5 ICSA1	Al	396.152	5571000	173.5		ppm	2/14/97	12:16:14
1	5	5 ICSA1	Mn	257.61	180.5	0.00837		ppm	2/14/97	12:16:36
1	5	5 ICSA1	Fe	259.94	1182000	192.2		ppm	2/14/97	12:17:00
1	5	5 ICSA1	Mg	279.079	481810	521.2		ppm	2/14/97	12:17:21
1	5	5 ICSA1	Ca	317.933	5147000	572.6		ppm	2/14/97	12:17:43
1	9	9 ICSA1	As	193.696	53.77	B.D.L.		ppm	2/14/97	12:19:24
1	9	9 ICSA1	Al	396.152	5765000	494.3		ppm	2/14/97	12:20:07
1	9	9 ICSA1	Mn	257.61	42850	0.4899		ppm	2/14/97	12:20:51
1	9	9 ICSA1	Fe	259.94	3245000	203.0		ppm	2/14/97	12:20:54
1	9	9 ICSA1	Mg	279.079	4932000	586.2		ppm	2/14/97	12:21:13
1	9	9 ICSA1	Ca	317.933	5225000	523		ppm	2/14/97	12:21:33
1	43	Method Blank	As	193.696	26.23	B.D.L.		ppm	2/14/97	12:23:18
1	43	Method Blank	Al	396.152	163.0	0.1872		ppm	2/14/97	12:23:02

Calibration of instrument

1	43 Method Blank	Mn	257.61	10.34	B.D.L.	ppm	2/14/97	12:21:23	
1	43 Method Blank	Fe	259.94	2769	0.0755	ppm	2/14/97	12:21:18	
1	43 Method Blank	Mg	259.94	1037	B.D.L.	ppm	2/14/97	12:25:17	
1	43 Method Blank	Cu	317.933	3028	B.D.L.	ppm	2/14/97	12:25:26	
1	44 Method Blank 1	As	193.696	2.106	B.D.L.	ppm	2/14/97	12:27:12	
1	44 Method Blank 1	Al	396.152	14940	0.19014	ppm	2/14/97	12:27:51	
1	44 Method Blank 1	Mn	257.61	1017	B.D.L.	ppm	2/14/97	12:28:18	
1	44 Method Blank 1	Fe	259.94	2152	0.07981	ppm	2/14/97	12:28:46	
1	44 Method Blank 1	Mg	279.079	906.8	B.D.L.	ppm	2/14/97	12:29:00	
1	44 Method Blank 1	Cu	317.933	4676	B.D.L.	ppm	2/14/97	12:29:16	
1	10 LCS (CCV)	As	193.696	173.1	0.4942	ppm	2/14/97	12:31:04	
1	10 LCS (CCV)	Al	396.152	14920	0.62	ppm	2/14/97	12:31:45	
1	10 LCS (CCV)	Mn	257.61	6427	0.2634	ppm	2/14/97	12:32:11	
1	10 LCS (CCV)	Fe	259.94	1966	5.017	ppm	2/14/97	12:32:14	
1	10 LCS (CCV)	Mg	279.079	23-20	238.4	ppm	2/14/97	12:32:54	
1	10 LCS (CCV)	Ca	317.933	259000	245.3	ppm	2/14/97	12:33:13	
1	1 254nm 30% H2O2 5K	As	193.696	23.86	B.D.L.	ppm	2/14/97	12:34:58	
1	1 254nm 30% H2O2 5K	Al	395.152	14830	0.08282	ppm	2/14/97	12:35:11	
1	1 254nm 30% H2O2 5K	Mn	257.61	5698	0.05184	ppm	2/14/97	12:36:05	
1	1 254nm 30% H2O2 5K	Fe	259.94	3094	0.2075	ppm	2/14/97	12:36:27	
1	1 254nm 30% H2O2 5K	Mg	279.079	1030	B.D.L.	ppm	2/14/97	12:36:47	
1	1 254nm 30% H2O2 5K	Ca	317.933	5429	B.D.L.	ppm	2/14/97	12:37:16	
1	2 254nm 30% H2O2 5K D	As	193.696	3974	B.D.L.	ppm	2/14/97	12:38:20	
1	2 254nm 30% H2O2 5K D	Al	396.152	14450	0.05603	ppm	2/14/97	12:38:33	
1	2 254nm 30% H2O2 5K D	Mn	257.61	5676	0.05159	ppm	2/14/97	12:39:27	
1	2 254nm 30% H2O2 5K D	Fe	259.94	5057	0.2051	ppm	2/14/97	12:40:20	
1	2 254nm 30% H2O2 5K D	Ni	279.079	977.6	B.D.L.	ppm	2/14/97	12:40:39	
1	2 254nm 30% H2O2 5K D	Ca	317.933	5272	B.D.L.	ppm	2/14/97	12:40:58	
1	3 254nm 30% H2O2 5K S	As	193.696	25.37	B.D.L.	ppm	2/14/97	12:42:43	
1	3 254nm 30% H2O2 5K S	Al	396.152	14590	0.06338	ppm	2/14/97	12:43:20	
1	3 254nm 30% H2O2 5K S	Mn	257.61	7505	0.07213	ppm	2/14/97	12:43:49	
1	3 254nm 30% H2O2 5K S	Fe	259.94	6202	0.2733	ppm	2/14/97	12:44:12	
1	3 254nm 30% H2O2 5K S	Mg	279.079	944.8	B.D.L.	ppm	2/14/97	12:44:32	
1	3 254nm 30% H2O2 5K S	Ca	317.933	4465	B.D.L.	ppm	2/14/97	12:44:51	
1	4 254nm 30% H2O2 5K L	As	193.696	22.77	4Xs B.D.L.	ppm	2/14/97	12:45:36	
1	4 254nm 30% H2O2 5K L	Al	396.152	13540	4X B.D.L.	ppm	2/14/97	12:47:18	
1	4 254nm 30% H2O2 5K L	Mn	257.61	2201	4X 0.01279	ppm	2/14/97	12:47:42	
1	4 254nm 30% H2O2 5K L	Fe	259.94	2456	4X 0.05764	ppm	2/14/97	12:48:05	
1	4 254nm 30% H2O2 5K L	Mg	279.079	1399.9	4X B.D.L.	ppm	2/14/97	12:48:24	
1	4 254nm 30% H2O2 5K L	Ca	317.933	3524	4X B.D.L.	ppm	2/14/97	12:48:43	
1	5 real spike conc.	As	193.696	0.3309	B.D.L.	ppm	2/14/97	12:50:24	
1	5 real spike conc.	Al	396.152	62980	0.491	ppm	2/14/97	12:51:11	
1	5 real spike conc.	Fe	259.94	15390	8.664	ppm	2/14/97	12:51:54	
1	5 real spike conc.	Mg	279.079	300.1	0.01865	ppm	2/14/97	12:52:17	
1	5 real spike conc.	Cu	317.933	3260	0.01929	ppm	2/14/97	12:52:36	
1	5 real spike conc.	Mn	257.61	42330	4X	0.4859	1.944 ppm	2/14/97	12:53:53
1	10 CCV1	As	193.696	173.1	0.5157	ppm	2/14/97	12:57:51	
1	10 CCV1	Al	396.152	139700	5.818	ppm	2/14/97	12:58:34	
1	10 CCV1	Mn	257.61	59430	0.7734	ppm	2/14/97	12:58:54	
1	10 CCV1	Fe	259.94	77810	4.756	ppm	2/14/97	12:59:20	
1	10 CCV1	Mg	279.079	214100	243.2	ppm	2/14/97	12:59:40	
1	10 CCV1	Ca	317.933	240000	237.4	ppm	2/14/97	12:59:59	
1	1 CCBI	As	193.696	17.81	B.D.L.	ppm	2/14/97	13:01:44	
1	1 CCBI	Al	396.152	14680	B.D.L.	ppm	2/14/97	13:02:27	
1	1 CCBI	Mn	257.61	1242	B.D.L.	ppm	2/14/97	13:02:51	
1	1 CCBI	Fe	259.94	1613	B.D.L.	ppm	2/14/97	13:03:14	
1	1 CCBI	Mg	279.079	955.4	B.D.L.	ppm	2/14/97	13:03:37	
1	1 CCBI	Ca	317.933	4082	B.D.L.	ppm	2/14/97	13:03:52	
1	6 254nm 30% H2O2 90min	As	193.696	1411	4.411	ppm	2/14/97	13:15:01	
1	6 254nm 30% H2O2 90min	Al	396.152	428400	252.8	ppm	2/14/97	13:15:11	
1	6 254nm 30% H2O2 90min	Mn	257.61	1.681-07	226.4	ppm	2/14/97	13:14:08	
1	6 254nm 30% H2O2 90min	Fe	259.94	1.140-07	58.4	ppm	2/14/97	13:14:18	
1	6 254nm 30% H2O2 90min	Mg	279.079	30580	46.2	ppm	2/14/97	13:15:17	
1	6 254nm 30% H2O2 90min	Ca	317.933	427800	455.5	ppm	2/14/97	13:16:08	
1	6 254nm 30% H2O2 90min	Fe	259.94	70400	100X 8.335	830.5 ppm	2/14/97	13:19:50	
1	6 254nm 30% H2O2 90min	Mn	257.61	25210	500X 0.5319	255.9 ppm	2/14/97	13:22:15	
1	7 Berkeley Pi. Water	As	193.696	2211	6.919	ppm	2/14/97	13:25:11	
1	7 Berkeley Pi. Water	Al	395.152	3882000	235.6	ppm	2/14/97	13:25:44	
1	7 Berkeley Pi. Water	Mg	279.079	405430	437.6	ppm	2/14/97	13:27:37	

Calibration of Instrument

1	7	Berkeley Fit Water	Ca	317.933	4900000		419.8		ppm	2/14/97	15:28:11
1	7	Berkeley Fit Water	Fe	259.94	249000	100X	12.17	1217	ppm	2/14/97	15:31:51
1	7	Berkeley Fit Water	Mn	257.61	50500	500X	0.3857	241.6	ppm	2/14/97	15:35:05
1	8	185/254nm 90min	As	193.695	2130		6.819		ppm	2/14/97	15:37:03
1	8	185/254nm 90min	Al	396.152	3980000		242.2		ppm	2/14/97	15:37:45
1	8	185/254nm 90min	Mg	279.079	192900		455		ppm	2/14/97	15:39:38
1	8	185/254nm 90min	Ca	317.933	4071000		439.5		ppm	2/14/97	15:40:19
1	8	185/254nm 90min	Fe	259.94	254600	100X	12.41	1244	ppm	2/14/97	15:43:53
1	8	185/254nm 90min	Mn	257.61	34050	500X	1.52	250	ppm	2/14/97	15:47:07
1	9	254nm 90min	As	193.695	212		6.633		ppm	2/14/97	15:49:03
1	9	254nm 90min	Al	396.152	3403000		230.4		ppm	2/14/97	15:49:46
1	9	254nm 90min	Mg	279.079	467700		431		ppm	2/14/97	15:51:29
1	9	254nm 90min	Ca	317.933	3972000		418.4		ppm	2/14/97	15:52:11
1	9	254nm 90min	Fe	259.94	347500	100X	12.69	1269	ppm	2/14/97	15:55:52
1	9	254nm 90min	Mn	257.61	32410	500X	0.2041	23.6	ppm	2/14/97	15:59:08
1	10	254nm TiO2 90min	As	193.695	205		6.448		ppm	2/14/97	16:01:02
1	10	254nm TiO2 90min	Al	396.152	3765000		227.8		ppm	2/14/97	16:01:47
1	10	254nm TiO2 90min	Mg	279.079	475600		438.1		ppm	2/14/97	16:03:40
1	10	254nm TiO2 90min	Ca	317.933	4936000		420.2		ppm	2/14/97	16:04:12
1	10	254nm TiO2 90min	Fe	259.94	225200	100X	11.19	1119	ppm	2/14/97	16:07:53
1	10	254nm TiO2 90min	Mn	257.61	30030	500X	0.4787	239.4	ppm	2/14/97	16:11:09
1	46	Method Blank 3	As	193.695	26.11				ppm	2/14/97	16:13:06
1	46	Method Blank 3	Al	396.152	4740				ppm	2/14/97	16:13:48
1	46	Method Blank 3	Mn	257.61	1154				ppm	2/14/97	16:14:12
1	46	Method Blank 3	Fe	259.94	1477				ppm	2/14/97	16:14:53
1	46	Method Blank 3	Mg	279.079	809.2				ppm	2/14/97	16:14:54
1	46	Method Blank 3	Ca	317.933	2292				ppm	2/14/97	16:15:13
1	10	CCV2	As	193.695	147.5		1.4566		ppm	2/14/97	16:16:59
1	10	CCV2	Al	396.152	136000		9.526		ppm	2/14/97	16:17:42
1	10	CCV2	Mn	257.61	15730		0.749		ppm	2/14/97	16:18:02
1	10	CCV2	Fe	259.94	75270		4.085		ppm	2/14/97	16:18:28
1	10	CCV2	Mg	279.079	208500		233.7		ppm	2/14/97	16:18:47
1	10	CCV2	Ca	317.933	2470000		233.5		ppm	2/14/97	16:19:07
1	1	CCB2	As	193.695	13.59				ppm	2/14/97	16:20:52
1	1	CCB2	Al	396.152	1440				ppm	2/14/97	16:21:35
1	1	CCB2	Mn	257.61	1139				ppm	2/14/97	16:21:59
1	1	CCB2	Fe	259.94	1471				ppm	2/14/97	16:22:12
1	1	CCB2	Mg	279.079	876.1				ppm	2/14/97	16:22:11
1	1	CCB2	Ca	317.933	2231				ppm	2/14/97	16:23:00

Calibration of instrument

Results exported from: Varian LIBERTY										
Result File TAQAQC215										
Output Format .DIF										
Match Sample Level										
Match Program										
Match Elements										
Date and Time YES										
Report Made ALL DATA										
Report Made = ALL DATA, Date and Time = YES										
Rack#	Tube#	Stmp.Lab.	El.	WT.	Elem	Conc	Dilute Conc	Units	Date	Time
1	1	BLANK	As	193.696	0.94	0		ppm	2/15/97	19:28:06
1	1	BLANK	Al	396.152	7884	0		ppm	2/15/97	19:28:43
1	1	BLANK	Mn	257.61	603.7	0		ppm	2/15/97	19:29:06
1	1	BLANK	Fe	259.94	927.5	0		ppm	2/15/97	19:29:29
1	1	BLANK	Mg	279.079	424.6	0		ppm	2/15/97	19:29:45
1	1	BLANK	Ca	317.933	1666	0		ppm	2/15/97	19:30:08
1	2	STANDARD 1	As	193.696	40.87	0.1		ppm	2/15/97	19:31:53
1	2	STANDARD 1	Al	396.152	48300	2		ppm	2/15/97	19:32:30
1	2	STANDARD 1	Mn	257.61	16800	0.15		ppm	2/15/97	19:32:55
1	2	STANDARD 1	Fe	259.94	23710	1.311		ppm	2/15/97	19:33:22
1	2	STANDARD 1	Mg	279.079	61340	49.95		ppm	2/15/97	19:33:42
1	2	STANDARD 1	Ca	317.933	481100	49.97		ppm	2/15/97	19:34:11
1	3	STANDARD 2	As	193.696	166.3	0.5		ppm	2/15/97	19:35:40
1	3	STANDARD 2	Al	396.152	151800	9.999		ppm	2/15/97	19:35:28
1	3	STANDARD 2	Mn	257.61	75950	0.7495		ppm	2/15/97	19:36:52
1	3	STANDARD 2	Fe	259.94	106500	3.03		ppm	2/15/97	19:37:13
1	3	STANDARD 2	Mg	279.079	289800	7.98		ppm	2/15/97	19:37:33
1	3	STANDARD 2	Ca	317.933	2268000	2.9.9		ppm	2/15/97	19:37:52
1	4	STANDARD 3	As	193.696	299.1	1		ppm	2/15/97	19:38:49
1	4	STANDARD 3	Al	396.152	547800	30		ppm	2/15/97	19:39:22
1	4	STANDARD 3	Mn	257.61	143000	1.499		ppm	2/15/97	19:40:46
1	4	STANDARD 3	Fe	259.94	154600	10.11		ppm	2/15/97	19:41:09
1	4	STANDARD 3	Mg	279.079	544300	499.5		ppm	2/15/97	19:41:28
1	4	STANDARD 3	Ca	317.933	4145000	499.7		ppm	2/15/97	19:41:47
1	5	STANDARD 4	Al	396.152	7261000	501.7		ppm	2/15/97	19:43:33
1	5	STANDARD 4	Fe	259.94	3965000	199.8		ppm	2/15/97	19:44:22
1	6	STANDARD 5	As	193.696	15810	50		ppm	2/15/97	19:46:19
1	7	ICV	As	193.696	3.28.5	1.877		ppm	2/15/97	19:48:29
1	7	ICV	Al	396.152	3703000	20.45		ppm	2/15/97	19:49:12
1	7	ICV	Me	257.61	1.7700	1.557		ppm	2/15/97	19:49:36
1	7	ICV	Fe	259.94	208900	10.07		ppm	2/15/97	19:49:58
1	7	ICV	Mg	279.079	577800	584.2		ppm	2/15/97	19:50:18
1	7	ICV	Ca	317.933	1399000	537.8		ppm	2/15/97	19:50:37
1	1	ICB	As	193.696	18.92	B.D.L.		ppm	2/15/97	19:52:23
1	1	ICB	Al	396.152	8161	B.D.L.		ppm	2/15/97	19:53:05
1	1	ICB	Mn	257.61	634.3	B.D.L.		ppm	2/15/97	19:53:29
1	1	ICB	Fe	259.94	1182	B.D.L.		ppm	2/15/97	19:53:52
1	1	ICB	Mg	279.079	506	B.D.L.		ppm	2/15/97	19:54:11
1	1	ICB	Ca	317.933	2181	B.D.L.		ppm	2/15/97	19:54:30
1	8	CRII	As	193.696	22.5	B.D.L.		ppm	2/15/97	19:56:15
1	8	CRII	Al	396.152	8257	B.D.L.		ppm	2/15/97	19:56:54
1	8	CRII	Mn	257.61	4492	0.0572		ppm	2/15/97	19:57:22
1	8	CRII	Fe	259.94	1316	0.01862		ppm	2/15/97	19:57:45
1	8	CRII	Mg	279.079	444.5	B.D.L.		ppm	2/15/97	19:58:04
1	8	CRII	Ca	317.933	2420	B.D.L.		ppm	2/15/97	19:58:23
1	5	ICSAI	As	193.696	40.34	0.0985		ppm	2/15/97	20:00:08
1	5	ICSAI	Al	396.152	7339000	510.5		ppm	2/15/97	20:00:51
1	5	ICSAI	Mn	257.61	1696	0.01001		ppm	2/15/97	20:01:33
1	5	ICSAI	Fe	259.94	3868000	195		ppm	2/15/97	20:02:05
1	5	ICSAI	Mg	279.079	514000	540.7		ppm	2/15/97	20:02:24
1	5	ICSAI	Ca	317.933	4346000	529.9		ppm	2/15/97	20:02:43
1	9	ICSAI	As	193.696	-26.31	B.D.L.		ppm	2/15/97	20:03:29
1	9	ICSAI	Al	396.152	7199000	484.4		ppm	2/15/97	20:03:53
1	9	ICSAI	Mn	257.61	40820	0.406		ppm	2/15/97	20:04:53
1	9	ICSAI	Fe	259.94	3797000	19.6		ppm	2/15/97	20:06:25
1	9	ICSAI	Mg	279.079	574700	530.9		ppm	2/15/97	20:06:43
1	9	ICSAI	Ca	317.933	2797000	510.5		ppm	2/15/97	20:07:03
1	44	Method Blank 1	As	193.696	15.55	B.D.L.		ppm	2/15/97	20:12:42
1	44	Method Blank 1	Al	396.152	5136	0.06159		ppm	2/15/97	20:13:25
1	44	Method Blank 1	Mn	257.61	575.6	B.D.L.		ppm	2/15/97	20:13:49

Calibration of Instrument:

1	44	Method Blank 1	Fe	259.94	1250		B.D.L.	ppm	2/15/97	20/14/1
1	44	Method Blank 1	Mg	279.079	507.6		B.D.L.	ppm	2/15/97	20/14/31
1	44	Method Blank 1	Ca	317.933	7247		B.D.L.	ppm	2/15/97	20/14/50
1	19	LCS (CCV)	As	193.696	168		0.3264	ppm	2/15/97	20/16/33
1	19	LCS (CCV)	Al	396.152	189800		9.574	ppm	2/15/97	20/17/18
1	19	LCS (CCV)	Mn	257.61	71800		0.7058	ppm	2/15/97	20/17/42
1	19	LCS (CCV)	Fe	259.94	103900		4.939	ppm	2/15/97	20/18/35
1	19	LCS (CCV)	Mg	279.079	278000		239	ppm	2/15/97	20/18/36
1	19	LCS (CCV)	Ca	317.933	2143000		235.3	ppm	2/15/97	20/18/43
1	1	254nm H2O2 1.25 SK	As	193.696	-8.33		B.D.L.	ppm	2/15/97	20/20/29
1	1	254nm H2O2 1.25 SK	Al	396.152	4971		107102	ppm	2/15/97	20/21/17
1	1	254nm H2O2 1.25 SK	Mn	257.61	5825		1008004	ppm	2/15/97	20/21/36
1	1	254nm H2O2 1.25 SK	Fe	259.94	4755		0.1848	ppm	2/15/97	20/21/58
1	1	254nm H2O2 1.25 SK	Mg	279.079	597.3		B.D.L.	ppm	2/15/97	20/22/18
1	1	254nm H2O2 1.25 SK	Ca	317.933	1086		B.D.L.	ppm	2/15/97	20/22/37
1	2	254nm H2O2 1.25 SK D	As	193.696	11.77		B.D.L.	ppm	2/15/97	20/24/22
1	2	254nm H2O2 1.25 SK D	Al	396.152	9027		0.05728	ppm	2/15/97	20/25/05
1	2	254nm H2O2 1.25 SK D	Mn	257.61	3817		0.04794	ppm	2/15/97	20/25/25
1	2	254nm H2O2 1.25 SK D	Fe	259.94	4677		0.1786	ppm	2/15/97	20/25/51
1	2	254nm H2O2 1.25 SK D	Mg	279.079	572.4		B.D.L.	ppm	2/15/97	20/26/11
1	2	254nm H2O2 1.25 SK D	Ca	317.933	2836		B.D.L.	ppm	2/15/97	20/26/38
1	3	254nm H2O2 1.25 SK S	As	193.696	12.8		B.D.L.	ppm	2/15/97	20/28/15
1	3	254nm H2O2 1.25 SK S	Al	396.152	9509		0.1985	ppm	2/15/97	20/28/58
1	3	254nm H2O2 1.25 SK S	Mn	257.61	8120		0.00925	ppm	2/15/97	20/29/22
1	3	254nm H2O2 1.25 SK S	Fe	259.94	6430		0.268	ppm	2/15/97	20/29/44
1	3	254nm H2O2 1.25 SK S	Mg	279.079	571.2		B.D.L.	ppm	2/15/97	20/30/84
1	3	254nm H2O2 1.25 SK S	Ca	317.933	7137		B.D.L.	ppm	2/15/97	20/30/71
1	4	254nm H2O2 1.25 SK L	As	193.696	5.599		B.D.L.	ppm	2/15/97	20/32/08
1	4	254nm H2O2 1.25 SK L	Al	396.152	8094	4X	0.000325	0.0253 ppm	2/15/97	20/32/51
1	4	254nm H2O2 1.25 SK L	Mn	257.61	1923	4X	0.01211	0.04843 ppm	2/15/97	20/33/3
1	4	254nm H2O2 1.25 SK L	Fe	259.94	1897	4X	0.04651	0.186 ppm	2/15/97	20/33/17
1	4	254nm H2O2 1.25 SK L	Mg	279.079	470.2	4X	0.003625	0.1478 ppm	2/15/97	20/33/37
1	4	254nm H2O2 1.25 SK L	Ca	317.933	2195	4X	0.05485	0.2194 ppm	2/15/97	20/34/6
1	10	CCV1	As	193.696	167.2		1.5237	ppm	2/15/97	20/36/01
1	10	CCV1	Al	396.152	185500		9.958	ppm	2/15/97	20/36/24
1	10	CCV1	Mn	257.61	73640		0.7147	ppm	2/15/97	20/37/08
1	10	CCV1	Fe	259.94	104000		4.987	ppm	2/15/97	20/37/30
1	10	CCV1	Mg	279.079	280700		241.5	ppm	2/15/97	20/37/50
1	10	CCV1	Ca	317.933	2182000		210	ppm	2/15/97	20/38/09
1		CCB1	As	193.696	12.76		B.D.L.	ppm	2/15/97	20/39/35
1		CCB1	Al	396.152	7994		B.D.L.	ppm	2/15/97	20/40/17
1		CCB1	Mn	257.61	6027		B.D.L.	ppm	2/15/97	20/41/04
1		CCB1	Fe	259.94	975.6		B.D.L.	ppm	2/15/97	20/41/24
1		CCB1	Mg	279.079	457.4		B.D.L.	ppm	2/15/97	20/41/44
1		CCB1	Ca	317.933	1969		B.D.L.	ppm	2/15/97	20/42/04
1	5	254nm H2O2 1.25mL O2	As	193.696	1561		2.166	ppm	2/15/97	20/43/47
1	5	254nm H2O2 1.25mL O2	Al	396.152	454000		282.7	ppm	2/15/97	20/44/59
1	5	254nm H2O2 1.25mL O2	Mg	279.079	529400		483.8	ppm	2/15/97	20/46/24
1	5	254nm H2O2 1.25mL O2	Ca	317.933	4008000		479.2	ppm	2/15/97	20/46/56
1	5	254nm H2O2 1.25mL O2	Fe	259.94	172200	100X	8.289	828.7 ppm	2/15/97	20/50/77
1	5	254nm H2O2 1.25mL O2	Mn	257.61	52740	500X	0.4095	219.9 ppm	2/15/97	20/53/34
1	6	254nm H2O2 0.25mL O2	As	193.696	1522		5.037	ppm	2/15/97	20/55/49
1	6	254nm H2O2 0.25mL O2	Al	396.152	4315000		265	ppm	2/15/97	20/56/32
1	6	254nm H2O2 0.25mL O2	Mg	279.079	515200		469.2	ppm	2/15/97	20/58/25
1	6	254nm H2O2 0.25mL O2	Ca	317.933	3970000		473.7	ppm	2/15/97	20/58/58
1	6	254nm H2O2 0.25mL O2	Fe	259.94	180000	100X	8.668	866.8 ppm	2/15/97	21/02/38
1	6	254nm H2O2 0.25mL O2	Mn	257.61	54540	500X	0.518	259 ppm	2/15/97	21/05/53
1	7	185/254nm H2O2 0.25mL	As	193.696	1486		4.919	ppm	2/15/97	21/07/80
1	7	185/254nm H2O2 0.25mL	Al	396.152	4134000		252.3	ppm	2/15/97	21/08/33
1	7	185/254nm H2O2 0.25mL	Mg	279.079	509500		463.4	ppm	2/15/97	21/10/26
1	7	185/254nm H2O2 0.25mL	Ca	317.933	3988000		476.4	ppm	2/15/97	21/10/58
1	7	185/254nm H2O2 0.25mL	Fe	259.94	1741000	100X	8.583	858.3 ppm	2/15/97	21/14/38
1	7	185/254nm H2O2 0.25mL	Mn	257.61	52870	500X	0.512	259 ppm	2/15/97	21/17/53
1	8	254nm O2	As	193.696	2252		7.439	ppm	2/15/97	21/19/80
1	8	254nm O2	Al	396.152	4017000		244.2	ppm	2/15/97	21/20/33
1	8	254nm O2	Mg	279.079	567100		460.8	ppm	2/15/97	21/22/20
1	8	254nm O2	Ca	317.933	3854000		462.7	ppm	2/15/97	21/23/58
1	8	254nm O2	Fe	259.94	251900	100X	12.16	1216 ppm	2/15/97	21/26/38
1	8	254nm O2	Mn	257.61	53710	500X	0.5196	254.8 ppm	2/15/97	21/29/54
1	8	CR12	As	193.696	4.188		13.11	ppm	2/15/97	21/31/51

Calibration of Instrument

1	8	CR12	Al	396.152	1223	H.D.L.	ppm	21/5/97	21:32:34
1	8	CR12	Mn	257.61	5645	0.04635	ppm	21/5/97	21:32:38
1	8	CR12	Fe	259.54	2620	0.08161	ppm	21/5/97	21:32:20
1	8	CR12	Mg	279.079	458.2	H.D.L.	ppm	21/5/97	21:32:40
1	8	CR12	Ca	317.933	2423	H.D.L.	ppm	21/5/97	21:32:35
1	5	ICSA2	As	193.656	52.94	0.1407	ppm	21/5/97	21:33:44
1	5	ICSA2	Al	396.152	6537000	415.2	ppm	21/5/97	21:36:27
1	5	ICSA2	Mn	257.61	2319	0.01572	ppm	21/5/97	21:37:05
1	5	ICSA2	Fe	259.54	3634000	115.7	ppm	21/5/97	21:37:41
1	5	ICSA2	Mg	279.079	548700	503.8	ppm	21/5/97	21:38:00
1	5	ICSA2	Ca	317.933	4252000	5.5.8	ppm	21/5/97	21:38:15
1	9	ICSAE2	As	193.656	41.36	H.D.L.	ppm	21/5/97	21:40:02
1	9	ICSAE2	Al	396.152	6537000	417.1	ppm	21/5/97	21:40:48
1	9	ICSAE2	Mn	257.61	45860	0.431	ppm	21/5/97	21:41:25
1	9	ICSAE2	Fe	259.54	3633000	144.6	ppm	21/5/97	21:42:01
1	9	ICSAE2	Mg	279.079	546600	501.7	ppm	21/5/97	21:42:20
1	9	ICSAE2	Ca	317.933	4157000	503	ppm	21/5/97	21:43:40
1	50	Method Blank 7	As	193.656	15.16	H.D.L.	ppm	21/5/97	22:01:50
1	50	Method Blank 7	Al	396.152	7752	H.D.L.	ppm	21/5/97	22:01:32
1	50	Method Blank 7	Mn	257.61	754.1	0.001458	ppm	21/5/97	22:01:56
1	50	Method Blank 7	Fe	259.54	957.9	H.D.L.	ppm	21/5/97	22:05:19
1	50	Method Blank 7	Mg	279.079	416.8	H.D.L.	ppm	21/5/97	22:05:39
1	50	Method Blank 7	Ca	317.933	1731	H.D.L.	ppm	21/5/97	22:05:54
1	10	CCV2	As	193.656	157.5	0.4909	ppm	21/5/97	22:07:43
1	10	CCV2	Al	396.152	177200	9.245	ppm	21/5/97	22:08:26
1	10	CCV2	Mn	257.61	70690	0.6817	ppm	21/5/97	22:08:56
1	10	CCV2	Fe	259.54	90040	4.74	ppm	21/5/97	22:09:11
1	10	CCV2	Mg	279.079	256100	228.1	ppm	21/5/97	22:09:32
1	10	CCV2	Ca	317.933	2113000	231.7	ppm	21/5/97	22:09:5
1	1	CCB2	As	193.656	11.64	H.D.L.	ppm	21/5/97	22:11:36
1	1	CCB2	Al	396.152	7631	H.D.L.	ppm	21/5/97	22:12:19
1	1	CCB2	Mn	257.61	639.8	H.D.L.	ppm	21/5/97	22:12:41
1	1	CCB2	Fe	259.54	977.9	H.D.L.	ppm	21/5/97	22:13:05
1	1	CCB2	Mg	279.079	409.1	H.D.L.	ppm	21/5/97	22:13:25
1	1	CCB2	Ca	317.933	1904	H.D.L.	ppm	21/5/97	22:13:44

Section 7.4. Analyze calibration standard (ICV)		10%						Section 8.5.2. Matrix spikes			
Acceptable Criteria		measured conc.	true value	%				Recovery	75% - 125%	Actual conc.	R %
As	1.131	1.004	1.004 ppm	12.65				As	B.D.L.	B.D.L.	
Al	20.01	20.055	ppm	-0.22				Al	0.03418	0.08129	
Mn	1.581	1.503	ppm	5.19				Mn	0.05264	0.0756	118
Fe	9.903	9.995	ppm	-0.92				Fe	0.1868	0.2743	102
Mg	514.4	500.828	ppm	2.71				Mg	B.D.L.	B.D.L.	
Ca	510	500.002	ppm	2.00				Ca	B.D.L.	B.D.L.	
Section 8.3. Method blank								Section 8.4. Analytical duplicates			
Acceptable Criteria		N/A						RPD		RPD = 100 * (C1-C2)/[(C1+C2)/2]	
As	measured conc.	C.R.D.L.	0.01 ppm					As	C1	C2	RPD %
Al	B.D.L.	0.04957	0.20 ppm					Al	B.D.L.	B.D.L.	
Mn	B.D.L.	0.015	ppm					Mn	0.07102	0.05728	
Fe	B.D.L.	0.10	ppm					Fe	0.03264	0.05235	0.55
Mg	B.D.L.	5.00	ppm					Mg	0.1868	0.185	0.97
Ca	B.D.L.	5.00	ppm					Ca	D.D.L.	B.D.L.	
Section 8.6.1.1. Check standard								Section 8.6.1.2. Calibration blank (CCB)			
Acceptable Criteria		10%						Acceptable Criteria			
As	measured conc.	true value	0.502 ppm	-8.15				As	measured co	C.R.D.L.	
Al	0.4596	10.03	ppm	-5.61				Al	B.D.L.	0.01 ppm	
Mn	9.465	0.752	ppm	-4.34				Mn	B.D.L.	0.20 ppm	
Fe	0.7194	5.00	ppm	-1.46				Fe	B.D.L.	0.015 ppm	
Mg	1.925	250.41	ppm	-5.16				Mg	B.D.L.	0.10 ppm	
Ca	237.2	250.00	ppm	-7.12				Ca	B.D.L.	5.00 ppm	
Ca	232.2	250.00	ppm	-7.12				Ca	B.D.L.	5.00 ppm	

Calibrator of Instrument

Results exported from Varian LIBERTY										
Result File: TAJQACC215										
Output Format: .DIF										
Match Sample Label:										
Match Program:										
Match Elements:										
Date and Time: YES										
Report Mode: ALL DATA										
Report Mode - ALL DATA Date and Time - YES										
Row#	Tube#	Samp. Lab.	El	WL	Intens	Conc	Dilute Con	Units	Date	Time
1	1	BLANK	As	193.696	22.12	0		ppm	2/16/97	18:00:48
1	1	BLANK	Al	396.152	10210	0		ppm	2/16/97	18:01:31
1	1	BLANK	Mn	257.61	836	0		ppm	2/16/97	18:01:55
1	1	BLANK	Fe	259.94	1180	0		ppm	2/16/97	18:02:18
1	1	BLANK	Mg	279.079	618.7	0		ppm	2/16/97	18:02:37
1	1	BLANK	Ca	317.933	2203	0		ppm	2/16/97	18:02:55
1	2	STANDARD 1	As	193.696	41.16	0.1		ppm	2/16/97	18:04:41
1	2	STANDARD 1	Al	396.152	35230	2		ppm	2/16/97	18:05:24
1	2	STANDARD 1	Mn	257.61	13980	0.15		ppm	2/16/97	18:05:48
1	2	STANDARD 1	Fe	259.94	18210	1.911		ppm	2/16/97	18:05:11
1	2	STANDARD 1	Mg	279.079	44320	49.65		ppm	2/16/97	18:05:39
1	2	STANDARD 1	Ca	317.933	424600	49.97		ppm	2/16/97	18:05:49
1	3	STANDARD 2	As	193.696	152.5	0.5		ppm	2/16/97	18:06:34
1	3	STANDARD 2	Al	396.152	121160	9.959		ppm	2/16/97	18:09:17
1	3	STANDARD 2	Mn	257.61	57460	0.7465		ppm	2/16/97	18:09:41
1	3	STANDARD 2	Fe	259.94	80650	5.65		ppm	2/16/97	18:10:04
1	3	STANDARD 2	Mg	279.079	209700	249.8		ppm	2/16/97	18:10:24
1	3	STANDARD 2	Ca	317.933	1968000	249.9		ppm	2/16/97	18:10:43
1	4	STANDARD 3	As	193.696	277.9	1		ppm	2/16/97	18:12:28
1	4	STANDARD 3	Al	396.152	219900	20		ppm	2/16/97	18:13:11
1	4	STANDARD 3	Mn	257.61	113100	1.499		ppm	2/16/97	18:13:33
1	4	STANDARD 3	Fe	259.94	150400	10.11		ppm	2/16/97	18:13:57
1	4	STANDARD 3	Mg	279.079	405900	400.5		ppm	2/16/97	18:14:17
1	4	STANDARD 3	Ca	317.933	7787000	493.7		ppm	2/16/97	18:14:36
1	5	STANDARD 4	Al	396.152	4783000	531.7		ppm	2/16/97	18:16:21
1	5	STANDARD 4	Fe	259.94	3008000	192.8		ppm	2/16/97	18:16:33
1	6	STANDARD 5	As	193.696	11520	50		ppm	2/16/97	18:18:42
1	7	KV	As	193.696	301.6	1.131		ppm	2/16/97	18:20:32
1	7	KV	Al	396.152	231000	23.01		ppm	2/16/97	18:21:35
1	7	KV	Mn	257.61	114500	1.581		ppm	2/16/97	18:21:59
1	7	KV	Fe	259.94	156200	9.503		ppm	2/16/97	18:22:21
1	7	KV	Mg	279.079	416500	514.4		ppm	2/16/97	18:22:41
1	7	KV	Ca	317.933	2830000	513		ppm	2/16/97	18:23:06
1	1	ICB	As	193.696	18.41	B.D.L.		ppm	2/16/97	18:23:15
1	1	ICB	Al	396.152	10340	B.D.L.		ppm	2/16/97	18:23:28
1	1	ICB	Mn	257.61	857.6	B.D.L.		ppm	2/16/97	18:23:32
1	1	ICB	Fe	259.94	1217	B.D.L.		ppm	2/16/97	18:23:44
1	1	ICB	Mg	279.079	663.2	B.D.L.		ppm	2/16/97	18:23:44
1	1	ICB	Ca	317.933	2525	B.D.L.		ppm	2/16/97	18:23:53
1	8	CR11	As	193.696	23.62	B.D.L.		ppm	2/16/97	18:28:38
1	8	CR11	Al	396.152	10373	B.D.L.		ppm	2/16/97	18:29:21
1	8	CR11	Mn	257.61	7721	0.03544		ppm	2/16/97	18:29:45
1	8	CR11	Fe	259.94	1372	B.D.L.		ppm	2/16/97	18:30:07
1	8	CR11	Mg	279.079	649.1	B.D.L.		ppm	2/16/97	18:30:27
1	8	CR11	Ca	317.933	2763	B.D.L.		ppm	2/16/97	18:30:46
1	5	ICSA1	As	193.696	69.15	0.1043		ppm	2/16/97	18:32:12
1	5	ICSA1	Al	396.152	4766000	506.5		ppm	2/16/97	18:33:14
1	5	ICSA1	Mn	257.61	1590	0.009247		ppm	2/16/97	18:33:38
1	5	ICSA1	Fe	259.94	3336000	202.3		ppm	2/16/97	18:34:04
1	5	ICSA1	Mg	279.079	4336000	537.3		ppm	2/16/97	18:34:21
1	5	ICSA1	Ca	317.933	3905000	521.5		ppm	2/16/97	18:34:39
1	9	ICSA1	As	193.696	193.6	0.3332		ppm	2/16/97	18:36:23
1	9	ICSA1	Al	396.152	4750000	498.7		ppm	2/16/97	18:37:18
1	9	ICSA1	Mn	257.61	38290	0.4766		ppm	2/16/97	18:37:32
1	9	ICSA1	Fe	259.94	3121000	208.2		ppm	2/16/97	18:37:54
1	9	ICSA1	Mg	279.079	412300	549		ppm	2/16/97	18:38:14
1	9	ICSA1	Ca	317.933	3905000	525.2		ppm	2/16/97	18:38:33
1	43	Method Blank	As	193.696	17.72	B.D.L.		ppm	2/16/97	18:40:18
1	43	Method Blank	Al	396.152	11380	0.08594		ppm	2/16/97	18:41:01

Calibration of Instrument

1	43	Method Blank	Mn	257.61	851.9	B.D.L.	ppm	2/16/97	18-11-25		
1	43	Method Blank	Fe	259.94	1601	6.02657	ppm	2/16/97	18-11-27		
1	43	Method Blank	Mg	279.079	713	B.D.L.	ppm	2/16/97	18-12-07		
1	43	Method Blank	Ca	317.933	2815	B.D.L.	ppm	2/16/97	18-12-26		
1	44	Method Blank 1	As	193.696	16.87	B.D.L.	ppm	2/16/97	18-12-11		
1	44	Method Blank 1	Al	396.152	10980	0.04957	ppm	2/16/97	18-12-14		
1	44	Method Blank 1	Mn	257.61	841.9	B.D.L.	ppm	2/16/97	18-12-18		
1	44	Method Blank 1	Fe	259.94	1573	B.D.L.	ppm	2/16/97	18-12-11		
1	44	Method Blank 1	Mg	279.079	669	B.D.L.	ppm	2/16/97	18-12-00		
1	44	Method Blank 1	Ca	317.933	2529	B.D.L.	ppm	2/16/97	18-12-19		
1	10	LCS (CCV)	As	193.696	154	0.5364	ppm	2/16/97	18-12-05		
1	10	LCS (CCV)	Al	396.152	123000	10.13	ppm	2/16/97	18-12-18		
1	10	LCS (CCV)	Mn	257.61	57510	0.7414	ppm	2/16/97	18-12-12		
1	10	LCS (CCV)	Fe	259.94	31170	5.106	ppm	2/16/97	18-12-14		
1	10	LCS (CCV)	Mg	279.079	219500	249.1	ppm	2/16/97	18-12-14		
1	10	LCS (CCV)	Ca	317.933	1936000	244.1	ppm	2/16/97	18-12-13		
1	1	365nm H2O2 .25 5K	As	193.696	11.49	E.D.L.	ppm	2/16/97	18-12-18		
1	1	365nm H2O2 .25 5K	Al	396.152	10810	0.03413	ppm	2/16/97	18-12-11		
1	1	365nm H2O2 .25 5K	Mn	257.61	5111	0.05264	ppm	2/16/97	18-12-15		
1	1	365nm H2O2 .25 5K	Fe	259.94	4114	0.1868	ppm	2/16/97	18-12-18		
1	1	365nm H2O2 .25 5K	Mg	279.079	753.4	B.D.L.	ppm	2/16/97	18-12-17		
1	1	365nm H2O2 .25 5K	Ca	317.933	3380	B.D.L.	ppm	2/16/97	18-12-16		
1	2	365nm H2O2 .25 5K D	As	193.696	10.83	B.D.L.	ppm	2/16/97	18-12-11		
1	2	365nm H2O2 .25 5K D	Al	396.152	10780	0.13182	ppm	2/16/97	18-12-14		
1	2	365nm H2O2 .25 5K D	Mn	257.61	5087	0.05233	ppm	2/16/97	18-12-18		
1	2	365nm H2O2 .25 5K D	Fe	259.94	4085	0.183	ppm	2/16/97	18-12-21		
1	2	365nm H2O2 .25 5K D	Mg	279.079	753.5	B.D.L.	ppm	2/16/97	18-12-14		
1	2	365nm H2O2 .25 5K D	Ca	317.933	3283	B.D.L.	ppm	2/16/97	18-12-19		
1	3	365nm H2O2 .25 5K S	As	193.696	5.927	B.D.L.	ppm	2/16/97	18-12-11		
1	3	365nm H2O2 .25 5K S	Al	396.152	13300	0.08129	ppm	2/16/97	19-00-27		
1	3	365nm H2O2 .25 5K S	Mn	257.61	4064	0.0756	ppm	2/16/97	19-00-31		
1	3	365nm H2O2 .25 5K S	Fe	259.94	5486	0.2743	ppm	2/16/97	19-01-13		
1	3	365nm H2O2 .25 5K S	Mg	279.079	734.1	B.D.L.	ppm	2/16/97	19-01-33		
1	3	365nm H2O2 .25 5K S	Ca	317.933	3256	B.D.L.	ppm	2/16/97	19-01-32		
1	4	365nm H2O2 .25 5K L	As	193.696	21.61	4X	B.D.L.	2/16/97	19-03-37		
1	4	365nm H2O2 .25 5K L	Al	396.152	12280	4X	B.D.L.	2/16/97	19-04-20		
1	4	365nm H2O2 .25 5K L	Mn	257.61	1890	4X	0.01294	0.05174	ppm	2/16/97	19-04-14
1	4	365nm H2O2 .25 5K L	Fe	259.94	1890	4X	0.04502	0.1801	ppm	2/16/97	19-05-06
1	4	365nm H2O2 .25 5K L	Mg	279.079	658.2	4X	B.D.L.	ppm	2/16/97	19-05-26	
1	4	365nm H2O2 .25 5K L	Ca	317.933	2630	4X	B.D.L.	ppm	2/16/97	19-05-15	
1	11	CCV1	As	193.696	156.3	1.5458	ppm	2/16/97	19-07-30		
1	11	CCV1	Al	396.152	122200	1.11	ppm	2/16/97	19-08-13		
1	11	CCV1	Mn	257.61	58740	3.7529	ppm	2/16/97	19-08-37		
1	11	CCV1	Fe	259.94	13310	5.115	ppm	2/16/97	19-09-00		
1	11	CCV1	Mg	279.079	210100	248.2	ppm	2/16/97	19-09-19		
1	11	CCV1	Ca	317.933	1960000	244.0	ppm	2/16/97	19-09-38		
1	1	CCB1	As	193.696	12.87	B.D.L.	ppm	2/16/97	19-11-24		
1	1	CCB1	Al	396.152	10130	B.D.L.	ppm	2/16/97	19-12-07		
1	1	CCB1	Mn	257.61	841.6	B.D.L.	ppm	2/16/97	19-12-31		
1	1	CCB1	Fe	259.94	1123	B.D.L.	ppm	2/16/97	19-12-33		
1	1	CCB1	Mg	279.079	626.2	B.D.L.	ppm	2/16/97	19-13-13		
1	1	CCB1	Ca	317.933	2253	B.D.L.	ppm	2/16/97	19-13-22		
1	5	365nm H2O2 .25ml. O2	As	193.696	1229	-0.834	ppm	2/16/97	19-15-17		
1	5	365nm H2O2 .25ml. O2	Al	396.152	2810000	274	ppm	2/16/97	19-15-00		
1	5	365nm H2O2 .25ml. O2	Mg	279.079	358100	-89.7	ppm	2/16/97	19-17-53		
1	5	365nm H2O2 .25ml. O2	Ca	317.933	3558000	-69.1	ppm	2/16/97	19-18-23		
1	5	365nm H2O2 .25ml. O2	Fe	259.94	38100	100X	8.767	876.7	ppm	2/16/97	19-22-03
1	5	365nm H2O2 .25ml. O2	Mn	257.61	42340	500X	0.5208	265.4	ppm	2/16/97	19-23-21
1	6	254nm TiO2 2g/1 O2	As	193.696	583.2	B.D.L.	ppm	2/16/97	19-27-14		
1	6	254nm TiO2 2g/1 O2	Al	396.152	2746000	267.2	ppm	2/16/97	19-28-00		
1	6	254nm TiO2 2g/1 O2	Mg	279.079	3994000	491.3	ppm	2/16/97	19-29-54		
1	6	254nm TiO2 2g/1 O2	Ca	317.933	3459000	454.3	ppm	2/16/97	19-30-26		
1	6	254nm TiO2 2g/1 O2	Fe	259.94	179700	100X	11.41	1.41	ppm	2/16/97	19-34-07
1	6	254nm TiO2 2g/1 O2	Mn	257.61	42810	500X	0.5366	268.3	ppm	2/16/97	19-37-22
1	7	254nm TiO2 2g/1 O2	As	193.696	-617.2	B.D.L.	ppm	2/16/97	19-39-18		
1	7	254nm TiO2 2g/1 O2	Al	396.152	2698000	262.1	ppm	2/16/97	19-40-31		
1	7	254nm TiO2 2g/1 O2	Mg	279.079	403000	496.3	ppm	2/16/97	19-41-54		
1	7	254nm TiO2 2g/1 O2	Ca	317.933	3489000	458.7	ppm	2/16/97	19-42-26		
1	7	254nm TiO2 2g/1 O2	Fe	259.94	179900	100X	11.43	1.43	ppm	2/16/97	19-46-07

Calibration of Instrument

1	7	254nm TiO ₂ 2g/1.07	Mn	257.61	42690	500X	0.5349	207.4	ppm	2/16/97	19:49:22
1	8	CR12	As	193.696	26.92		B.D.L.		ppm	2/16/97	19:51:18
1	8	CR12	Al	396.152	13.30		B.D.L.		ppm	2/16/97	19:52:01
1	8	CR12	Mn	257.61	4236		0.04154		ppm	2/16/97	19:52:25
1	8	CR12	Fe	259.94	1911		0.04627		ppm	2/16/97	19:52:48
1	8	CR12	Mg	279.079	608.3		B.D.L.		ppm	2/16/97	19:53:07
1	8	CR12	Ca	317.933	25.78		B.D.L.		ppm	2/16/97	19:53:26
1	5	CSA2	As	193.696	76.55		B.D.L.		ppm	2/16/97	19:55:12
1	5	CSA2	Al	396.152	4395000		454.6		ppm	2/16/97	19:55:55
1	5	CSA2	Mn	257.61	1901		0.1118		ppm	2/16/97	19:56:18
1	5	CSA2	Fe	259.94	2867000		150.5		ppm	2/16/97	19:56:11
1	5	CSA2	Mg	279.079	110900		516.8		ppm	2/16/97	19:57:01
1	5	CSA2	Ca	317.933	3098000		459.1		ppm	2/16/97	19:57:19
1	9	ICSAB2	As	193.696	7.638		B.D.L.		ppm	2/16/97	19:59:05
1	9	ICSAB2	Al	396.152	4456000		461.9		ppm	2/16/97	19:59:48
1	9	ICSAB2	Mn	257.61	36570		0.4558		ppm	2/16/97	20:00:12
1	9	ICSAB2	Fe	259.94	2890000		192.2		ppm	2/16/97	20:00:35
1	9	ICSAB2	Mg	279.079	400600		565.1		ppm	2/16/97	20:00:54
1	9	ICSAB2	Ca	317.933	3664000		485		ppm	2/16/97	20:01:14
1	51	Method Blank 8	As	193.696	3.82		B.D.L.		ppm	2/16/97	20:06:17
1	51	Method Blank 8	Al	396.152	9766		B.D.L.		ppm	2/16/97	20:07:00
1	51	Method Blank 8	Mn	257.61	898.8		B.D.L.		ppm	2/16/97	20:07:23
1	51	Method Blank 8	Fe	259.94	1052		B.D.L.		ppm	2/16/97	20:07:46
1	51	Method Blank 8	Mg	279.079	591.2		B.D.L.		ppm	2/16/97	20:08:06
1	51	Method Blank 8	Ca	317.933	2078		B.D.L.		ppm	2/16/97	20:08:25
1	10	CCV2	As	193.696	134.9		0.4596		ppm	2/16/97	20:09:10
1	10	CCV2	Al	396.152	115100		9.165		ppm	2/16/97	20:09:52
1	10	CCV2	Mn	257.61	56310		0.7194		ppm	2/16/97	20:10:16
1	10	CCV2	Fe	259.94	78340		4.925		ppm	2/16/97	20:10:39
1	10	CCV2	Mg	279.079	201400		237.3		ppm	2/16/97	20:11:58
1	10	CCV2	Ca	317.933	1866000		222.3		ppm	2/16/97	20:12:18
1	1	CCB2	As	193.696	15.77		B.D.L.		ppm	2/16/97	20:14:03
1	1	CCB2	Al	396.152	9600		B.D.L.		ppm	2/16/97	20:14:46
1	1	CCB2	Mn	257.61	832.7		B.D.L.		ppm	2/16/97	20:15:10
1	1	CCB2	Fe	259.94	1165		B.D.L.		ppm	2/16/97	20:15:32
1	1	CCB2	Mg	279.079	582		B.D.L.		ppm	2/16/97	20:15:51
1	1	CCB2	Ca	317.933	2192		B.D.L.		ppm	2/16/97	20:16:11

QC Procedures

Section 7.4. Analyze calibration standard (ICV)		10%				Section 8.5.2 Matrix spikes			
Acceptable Criteria		measured conc.	true value	%		75% - 125%		%R = 100 * (S-U)/C	
As	0.9399	1.004	ppm	-6.38		Unspike (U)	Spike (S)	Actual conc.	R %
Al	19.44	20.055	ppm	-3.07		B.D.L.	B.D.L.		
Mn	1.468	1.503	ppm	-2.33		0.02279	0.06703		
Fe	9.401	9.995	ppm	-5.94		0.04519	0.06585	0.0194	106
Mg	500.1	500.828	ppm	-0.15		0.1688	0.2594	0.086	105
Ca	496.3	500.002	ppm	-0.74		B.D.L.	B.D.L.		
						B.D.L.	B.D.L.		
Section 8.3. Method blank									
Acceptable Criteria		N/A				Analytical duplicates		RPD = 100 * (C1-C2)/[(C1+C2)/2]	
						≤ 20%			
As	measured conc.	C.R.D.L.				CI	C2	RPD %	
Al	B.D.L.	0.01	ppm			B.D.L.	B.D.L.		
Mn	B.D.L.	0.20	ppm			0.02279	0.02032		
Fe	B.D.L.	0.015	ppm			0.04519	0.04492	0.60	
Mg	B.D.L.	5.00	ppm			0.1688	0.1701	-0.77	
Ca	B.D.L.	5.00	ppm			B.D.L.	B.D.L.		
						B.D.L.	B.D.L.		
Section 8.6.1.1. Check standard									
Acceptable Criteria		10%				Section 8.6.1.2. Calibration blank (CCB)			
						Acceptable Criteria			
As	measured conc.	true value				measured conc.	C.R.D.L.		
Al	0.4718	0.302	ppm	-6.02		B.D.L.	0.01	ppm	
Mn	9.874	10.03	ppm	-1.54		B.D.L.	0.20	ppm	
Fe	0.6942	0.757	ppm	-7.69		B.D.L.	0.015	ppm	
Mg	4.769	5.00	ppm	-4.58		B.D.L.	0.10	ppm	
Ca	235.6	250.41	ppm	-5.91		B.D.L.	5.00	ppm	
	233.8	250.00	ppm	-6.48		B.D.L.	5.00	ppm	

Calibration of Instrument

Results exported from Varian LIBERTY										
Result File TAIQAQC300										
Output Format D/F										
Match Sample Label										
Match Program										
Match Elements										
Date and Time YES										
Report Mode ALL DATA										
Report Mode = ALL DATA, Date and Time = YES										
Rack#	Tube#	Samp. Lab.	El	Wt.	Intens	Conc	Dilute Con	Units	Date	Time
1	1	BLANK	As	193.696	14.83	0		ppm	3/6/97	19:59:23
1	1	BLANK	Al	396.152	15310	0		ppm	3/6/97	20:00:02
1	1	BLANK	Mn	257.61	1223	0		ppm	3/6/97	20:00:25
1	1	BLANK	Fe	259.94	1423	0		ppm	3/6/97	20:00:49
1	1	BLANK	Mg	279.079	876.8	0		ppm	3/6/97	20:01:05
1	1	BLANK	Ca	317.933	2867	0		ppm	3/6/97	20:01:27
1	2	STANDARD 1	As	193.696	50.75	0.1		ppm	3/6/97	20:08:12
1	2	STANDARD 1	Al	396.152	53120	2		ppm	3/6/97	20:08:55
1	2	STANDARD 1	Mn	257.61	16080	0.15		ppm	3/6/97	20:09:19
1	2	STANDARD 1	Fe	259.94	21330	1.011		ppm	3/6/97	20:09:42
1	2	STANDARD 1	Mg	279.079	55820	49.95		ppm	3/6/97	20:05:01
1	2	STANDARD 1	Ca	317.933	678100	49.97		ppm	3/6/97	20:05:20
1	3	STANDARD 2	As	193.696	165	0.5		ppm	3/6/97	20:07:05
1	3	STANDARD 2	Al	396.152	191800	5.999		ppm	3/6/97	20:07:48
1	3	STANDARD 2	Mn	257.61	73460	0.7495		ppm	3/6/97	20:08:12
1	3	STANDARD 2	Fe	259.94	97800	5.05		ppm	3/6/97	20:08:35
1	3	STANDARD 2	Mg	279.079	269700	249.8		ppm	3/6/97	20:08:54
1	3	STANDARD 2	Ca	317.933	3258300	249.9		ppm	3/6/97	20:09:13
1	4	STANDARD 3	As	193.696	295.4	1		ppm	3/6/97	20:10:59
1	4	STANDARD 3	Al	396.152	125400	20		ppm	3/6/97	20:11:41
1	4	STANDARD 3	Mn	257.61	135200	1.499		ppm	3/6/97	20:12:05
1	4	STANDARD 3	Fe	259.94	177300	10.11		ppm	3/6/97	20:12:24
1	4	STANDARD 3	Mg	279.079	514900	499.5		ppm	3/6/97	20:12:43
1	4	STANDARD 3	Ca	317.933	5930000	499.7		ppm	3/6/97	20:13:07
1	5	STANDARD 4	Al	396.152	6439000	501.7		ppm	3/6/97	20:14:53
1	5	STANDARD 4	Fe	259.94	3585000	199.8		ppm	3/6/97	20:15:42
1	6	STANDARD 5	As	193.696	14560	50		ppm	3/6/97	20:17:39
1	7	KCV	As	193.696	296.6	0.9399		ppm	3/6/97	20:19:49
1	7	KCV	Al	396.152	341800	19.44		ppm	3/6/97	20:20:32
1	7	KCV	Mn	257.61	139000	1.408		ppm	3/6/97	20:20:56
1	7	KCV	Fe	259.94	76100	5.401		ppm	3/6/97	20:21:19
1	7	KCV	Mg	279.079	515300	500.1		ppm	3/6/97	20:21:33
1	7	KCV	Ca	317.933	5900000	496.3		ppm	3/6/97	20:21:57
1	1	ICB	As	193.696	11.42	B.D.L.		ppm	3/6/97	20:23:43
1	1	ICB	Al	396.152	15040	B.D.L.		ppm	3/6/97	20:24:26
1	1	ICB	Mn	257.61	1222	B.D.L.		ppm	3/6/97	20:24:50
1	1	ICB	Fe	259.94	1423	B.D.L.		ppm	3/6/97	20:25:12
1	1	ICB	Mg	279.079	879.4	B.D.L.		ppm	3/6/97	20:25:32
1	1	ICB	Ca	317.933	3146	B.D.L.		ppm	3/6/97	20:25:51
1	8	CRJ1	As	193.696	18.69	B.D.L.		ppm	3/6/97	20:27:36
1	8	CRJ1	Al	396.152	15100	B.D.L.		ppm	3/6/97	20:28:19
1	8	CRJ1	Mn	257.61	4690	1.03494		ppm	3/6/97	20:28:42
1	8	CRJ1	Fe	259.94	1713	1.01535		ppm	3/6/97	20:29:05
1	8	CRJ1	Mg	279.079	837.9	B.D.L.		ppm	3/6/97	20:29:24
1	8	CRJ1	Ca	317.933	3407	B.D.L.		ppm	3/6/97	20:29:43
1	5	ICSA1	As	193.696	147.1	0.4404		ppm	3/6/97	20:31:29
1	5	ICSA1	Al	396.152	6440000	503.7		ppm	3/6/97	20:32:11
1	5	ICSA1	Mn	257.61	2082	0.001654		ppm	3/6/97	20:32:53
1	5	ICSA1	Fe	259.94	3490000	194.3		ppm	3/6/97	20:33:24
1	5	ICSA1	Mg	279.079	545700	533.4		ppm	3/6/97	20:33:44
1	5	ICSA1	Ca	317.933	610000	519.8		ppm	3/6/97	20:34:01
1	9	ICSA1	As	193.696	-20.16	B.D.L.		ppm	3/6/97	20:35:49
1	9	ICSA1	Al	396.152	6617000	523.7		ppm	3/6/97	20:36:31
1	9	ICSA1	Mn	257.61	48130	0.4792		ppm	3/6/97	20:37:15
1	9	ICSA1	Fe	259.94	3178000	200		ppm	3/6/97	20:37:45
1	9	ICSA1	Mg	279.079	557600	546.4		ppm	3/6/97	20:38:04
1	9	ICSA1	Ca	317.933	6461000	559.1		ppm	3/6/97	20:38:23
1	-43	Method Blank	As	193.696	14.6	B.D.L.		ppm	3/6/97	20:41:50
1	-43	Method Blank	Al	396.152	15150	B.D.L.		ppm	3/6/97	20:44:33
1	-43	Method Blank	Mn	257.61	1.42	B.D.L.		ppm	3/6/97	20:44:57
1	-43	Method Blank	Fe	259.94	1136	B.D.L.		ppm	3/6/97	20:45:20
1	-43	Method Blank	Mg	279.079	876.6	B.D.L.		ppm	3/6/97	20:45:39
1	-43	Method Blank	Ca	317.933	3658	B.D.L.		ppm	3/6/97	20:45:58
1	-44	Method Blank 1	As	193.696	19.22	B.D.L.		ppm	3/6/97	20:47:46

Calibration of Instrument

44	Method Blank 1	Al	396.152	15360	B.D.L.	ppm	3/6/97	20:48:27	
44	Method Blank 1	Mn	257.61	1124	B.D.L.	ppm	3/6/97	20:48:51	
44	Method Blank 1	Fe	259.94	1296	B.D.L.	ppm	3/6/97	20:49:13	
44	Method Blank 1	Mg	279.079	859.5	B.D.L.	ppm	3/6/97	20:49:33	
44	Method Blank 1	Ca	317.933	3846	B.D.L.	ppm	3/6/97	20:49:52	
10	LCS (CCV)	As	193.696	162.4	0.4913	ppm	3/6/97	20:51:37	
10	LCS (CCV)	Al	396.152	173500	9.166	ppm	3/6/97	20:52:20	
10	LCS (CCV)	Mn	257.61	66660	0.6757	ppm	3/6/97	20:52:44	
10	LCS (CCV)	Fe	259.94	39070	4.712	ppm	3/6/97	20:53:07	
10	LCS (CCV)	Mg	279.079	249700	230.6	ppm	3/6/97	20:53:26	
10	LCS (CCV)	Ca	317.933	2968000	226.3	ppm	3/6/97	20:53:45	
1	No-UV H2O2 O2 1K	As	193.696	19.93	B.D.L.	ppm	3/6/97	20:55:31	
1	No-UV H2O2 O2 1K	Al	396.152	5990	0.02279	ppm	3/6/97	20:56:13	
1	No-UV H2O2 O2 1K	Mn	257.61	5707	0.04319	ppm	3/6/97	20:56:37	
1	No-UV H2O2 O2 1K	Fe	259.94	4599	0.1688	ppm	3/6/97	20:57:00	
1	No-UV H2O2 O2 1K	Mg	279.079	956	B.D.L.	ppm	3/6/97	20:57:19	
1	No-UV H2O2 O2 1K	Ca	317.933	4429	B.D.L.	ppm	3/6/97	20:57:39	
2	No-UV H2O2 O2 1K D	As	193.696	16.43	B.D.L.	ppm	3/6/97	20:59:24	
2	No-UV H2O2 O2 1K D	Al	396.152	5990	0.02032	ppm	3/6/97	21:00:06	
2	No-UV H2O2 O2 1K D	Mn	257.61	5680	0.04492	ppm	3/6/97	21:00:30	
2	No-UV H2O2 O2 1K D	Fe	259.94	4595	3.1701	ppm	3/6/97	21:00:53	
2	No-UV H2O2 O2 1K D	Mg	279.079	956.8	B.D.L.	ppm	3/6/97	21:01:12	
2	No-UV H2O2 O2 1K D	Ca	317.933	4328	B.D.L.	ppm	3/6/97	21:01:31	
3	No-UV H2O2 O2 1K S	As	193.696	8.252	B.D.L.	ppm	3/6/97	21:03:16	
3	No-UV H2O2 O2 1K S	Al	396.152	6740	0.06703	ppm	3/6/97	21:03:59	
3	No-UV H2O2 O2 1K S	Mn	257.61	7754	0.06385	ppm	3/6/97	21:04:22	
3	No-UV H2O2 O2 1K S	Fe	259.94	6237	3.2394	ppm	3/6/97	21:04:45	
3	No-UV H2O2 O2 1K S	Mg	279.079	956.4	B.D.L.	ppm	3/6/97	21:05:05	
3	No-UV H2O2 O2 1K S	Ca	317.933	4511	B.D.L.	ppm	3/6/97	21:05:24	
4	No-UV H2O2 O2 1K L	As	193.696	12.33	4X	B.D.L.	ppm	21:07:09	
4	No-UV H2O2 O2 1K L	Al	396.152	15280	4X	B.D.L.	ppm	21:07:51	
4	No-UV H2O2 O2 1K L	Mn	257.61	2252	4X	0.01036	0.04145	ppm	21:08:15
4	No-UV H2O2 O2 1K L	Fe	259.94	2183	4X	0.04056	0.1622	ppm	21:08:38
4	No-UV H2O2 O2 1K L	Mg	279.079	861.2	4X	B.D.L.	ppm	21:08:57	
4	No-UV H2O2 O2 1K L	Ca	317.933	3552	4X	B.D.L.	ppm	21:09:16	
10	CCV1	As	193.696	166.2	0.3943	ppm	3/6/97	21:11:02	
10	CCV1	Al	396.152	182100	9.177	ppm	3/6/97	21:11:44	
10	CCV1	Mn	257.61	68690	0.6972	ppm	3/6/97	21:12:08	
10	CCV1	Fe	259.94	92630	4.905	ppm	3/6/97	21:12:31	
10	CCV1	Mg	279.079	262500	242.8	ppm	3/6/97	21:12:50	
10	CCV1	Ca	317.933	3072000	234.8	ppm	3/6/97	21:13:09	
1	CCB1	As	193.696	21.18	B.D.L.	ppm	3/6/97	21:14:55	
1	CCB1	Al	396.152	14890	B.D.L.	ppm	3/6/97	21:15:37	
1	CCB1	Mn	257.61	1182	B.D.L.	ppm	3/6/97	21:16:01	
1	CCB1	Fe	259.94	1345	B.D.L.	ppm	3/6/97	21:16:24	
1	CCB1	Mg	279.079	855.2	B.D.L.	ppm	3/6/97	21:16:43	
1	CCB1	Ca	317.933	2930	B.D.L.	ppm	3/6/97	21:17:02	
5	No-UV 30% H2O2 O2(19)	As	193.696	1217	4.088	ppm	3/6/97	21:18:47	
5	No-UV 30% H2O2 O2(19)	Al	396.152	3691080	246.8	ppm	3/6/97	21:19:30	
5	No-UV 30% H2O2 O2(19)	Mg	279.079	477990	439.6	ppm	3/6/97	21:21:23	
5	No-UV 30% H2O2 O2(19)	Ca	317.933	5114080	421.6	ppm	3/6/97	21:21:55	
5	No-UV 30% H2O2 O2(19)	Fe	259.94	156180	100X	8.321	332.1	ppm	21:25:37
5	No-UV 30% H2O2 O2(19)	Mn	257.61	60580	400X	0.6097	243.9	ppm	21:28:54
6	No-UV O2 (sample 18)	As	193.696	1638	5.503	ppm	3/6/97	21:30:51	
6	No-UV O2 (sample 18)	Al	396.152	3766000	248	ppm	3/6/97	21:31:34	
6	No-UV O2 (sample 18)	Mg	279.079	464200	445.1	ppm	3/6/97	21:33:27	
6	No-UV O2 (sample 18)	Ca	317.933	3271000	433.2	ppm	3/6/97	21:33:58	
6	No-UV O2 (sample 18)	Fe	259.94	260100	100X	10.69	1069	ppm	21:37:39
6	No-UV O2 (sample 18)	Mn	257.61	57390	400X	0.5766	230.6	ppm	21:40:56
7	No-UV 30% H2O2 (s 17)	As	193.696	1196	3.552	ppm	3/6/97	21:42:53	
7	No-UV 30% H2O2 (s 17)	Al	396.152	3755000	253.4	ppm	3/6/97	21:43:35	
7	No-UV 30% H2O2 (s 17)	Mg	279.079	470900	452.2	ppm	3/6/97	21:45:28	
7	No-UV 30% H2O2 (s 17)	Ca	317.933	5370000	443.1	ppm	3/6/97	21:46:30	
7	No-UV 30% H2O2 (s 17)	Fe	259.94	149200	100X	7.551	795.1	ppm	21:49:41
7	No-UV 30% H2O2 (s 17)	Mn	257.61	58630	400X	0.5897	235.9	ppm	21:52:59
8	CR12	As	193.696	16.19	B.D.L.	ppm	3/6/97	21:54:56	
8	CR12	Al	396.152	15090	B.D.L.	ppm	3/6/97	21:55:58	
8	CR12	Mn	257.61	4465	0.03267	ppm	3/6/97	21:56:32	
8	CR12	Fe	259.94	1686	0.01391	ppm	3/6/97	21:56:25	
8	CR12	Mg	279.079	829.4	B.D.L.	ppm	3/6/97	21:56:45	
8	CR12	Ca	317.933	3470	B.D.L.	ppm	3/6/97	21:57:04	
5	JCSA2	As	193.696	1.91	B.D.L.	ppm	3/6/97	21:58:49	
5	JCSA2	Al	396.152	16860	0.07413	ppm	3/6/97	21:59:32	
5	JCSA2	Mn	257.61	1184	B.D.L.	ppm	3/6/97	21:59:36	

Calibration of Instrument

1	5 ICSA2	Fe	259.94	1342	B.D.L.	ppm	3/6/97	22:00:18
1	5 ICSA2	Mg	279.079	230500	2123	ppm	3/6/97	22:00:38
1	5 ICSA2	Ca	317.933	6256000	5362	ppm	3/6/97	22:00:57
1	9 ICSAB2	As	193.696	-1128	B.D.L.	ppm	3/6/97	22:02:42
1	9 ICSAB2	Al	396.152	6205000	4765	ppm	3/6/97	22:03:25
1	9 ICSAB2	Mn	257.61	45190	0.4484	ppm	3/6/97	22:04:06
1	9 ICSAB2	Fe	259.94	3291000	1833	ppm	3/6/97	22:04:38
1	9 ICSAB2	Mg	279.079	529900	5161	ppm	3/6/97	22:04:58
1	9 ICSAB2	Ca	317.933	6362000	5145	ppm	3/6/97	22:05:17
1	45 Method Blank 2	As	193.696	14.22	B.D.L.	ppm	3/6/97	22:07:03
1	45 Method Blank 2	Al	396.152	15470	B.D.L.	ppm	3/6/97	22:07:46
1	45 Method Blank 2	Mn	257.61	1266	B.D.L.	ppm	3/6/97	22:08:10
1	45 Method Blank 2	Fe	259.94	1447	B.D.L.	ppm	3/6/97	22:08:32
1	45 Method Blank 2	Mg	279.079	848.5	B.D.L.	ppm	3/6/97	22:08:52
1	45 Method Blank 2	Ca	317.933	5395	B.D.L.	ppm	3/6/97	22:09:11
1	46 Method Blank 3	As	193.696	18.11	B.D.L.	ppm	3/6/97	22:10:56
1	46 Method Blank 3	Al	396.152	14850	B.D.L.	ppm	3/6/97	22:11:38
1	46 Method Blank 3	Mn	257.61	1201	B.D.L.	ppm	3/6/97	22:12:02
1	46 Method Blank 3	Fe	259.94	1302	B.D.L.	ppm	3/6/97	22:12:25
1	46 Method Blank 3	Mg	279.079	822.5	B.D.L.	ppm	3/6/97	22:12:44
1	46 Method Blank 3	Ca	317.933	5082	B.D.L.	ppm	3/6/97	22:13:03
1	47 Method Blank 4	As	193.696	15.74	B.D.L.	ppm	3/6/97	22:14:48
1	47 Method Blank 4	Al	396.152	14740	B.D.L.	ppm	3/6/97	22:15:31
1	47 Method Blank 4	Mn	257.61	1190	B.D.L.	ppm	3/6/97	22:15:54
1	47 Method Blank 4	Fe	259.94	1301	B.D.L.	ppm	3/6/97	22:16:17
1	47 Method Blank 4	Mg	279.079	816.4	B.D.L.	ppm	3/6/97	22:16:36
1	47 Method Blank 4	Ca	317.933	5025	B.D.L.	ppm	3/6/97	22:16:56
1	48 Method Blank 5	As	193.696	15.91	B.D.L.	ppm	3/6/97	22:18:41
1	48 Method Blank 5	Al	396.152	14730	B.D.L.	ppm	3/6/97	22:19:23
1	48 Method Blank 5	Mn	257.61	1131	B.D.L.	ppm	3/6/97	22:19:47
1	48 Method Blank 5	Fe	259.94	1309	B.D.L.	ppm	3/6/97	22:20:10
1	48 Method Blank 5	Mg	279.079	823.4	B.D.L.	ppm	3/6/97	22:20:30
1	48 Method Blank 5	Ca	317.933	5207	B.D.L.	ppm	3/6/97	22:20:48
1	49 Method Blank 6	As	193.696	1502	B.D.L.	ppm	3/6/97	22:22:33
1	49 Method Blank 6	Al	396.152	14720	B.D.L.	ppm	3/6/97	22:23:16
1	49 Method Blank 6	Mn	257.61	1141	B.D.L.	ppm	3/6/97	22:23:40
1	49 Method Blank 6	Fe	259.94	1273	B.D.L.	ppm	3/6/97	22:24:03
1	49 Method Blank 6	Mg	279.079	820.3	B.D.L.	ppm	3/6/97	22:24:22
1	49 Method Blank 6	Ca	317.933	2914	B.D.L.	ppm	3/6/97	22:24:41
1	50 Method Blank 7	As	193.696	13.11	B.D.L.	ppm	3/6/97	22:26:26
1	50 Method Blank 7	Al	396.152	14700	B.D.L.	ppm	3/6/97	22:27:09
1	50 Method Blank 7	Mn	257.61	1152	B.D.L.	ppm	3/6/97	22:27:33
1	50 Method Blank 7	Fe	259.94	1259	B.D.L.	ppm	3/6/97	22:27:55
1	50 Method Blank 7	Mg	279.079	808.2	B.D.L.	ppm	3/6/97	22:28:15
1	50 Method Blank 7	Ca	317.933	5971	B.D.L.	ppm	3/6/97	22:28:34
1	51 Method Blank 8	As	193.696	12.32	B.D.L.	ppm	3/6/97	22:30:19
1	51 Method Blank 8	Al	396.152	16530	B.D.L.	ppm	3/6/97	22:31:01
1	51 Method Blank 8	Mn	257.61	1139	B.D.L.	ppm	3/6/97	22:31:25
1	51 Method Blank 8	Fe	259.94	1212	B.D.L.	ppm	3/6/97	22:31:48
1	51 Method Blank 8	Mg	279.079	891.3	B.D.L.	ppm	3/6/97	22:32:07
1	51 Method Blank 8	Ca	317.933	2981	B.D.L.	ppm	3/6/97	22:32:27
1	10 CCV2	As	193.696	156.5	0.4718	ppm	3/6/97	22:34:12
1	10 CCV2	Al	396.152	182000	9.874	ppm	3/6/97	22:34:55
1	10 CCV2	Mn	257.61	68370	0.6942	ppm	3/6/97	22:35:19
1	10 CCV2	Fe	259.94	90130	4.769	ppm	3/6/97	22:35:41
1	10 CCV2	Mg	279.079	254900	235.6	ppm	3/6/97	22:36:01
1	10 CCV2	Ca	317.933	3061000	233.8	ppm	3/6/97	22:36:20
1	1 CCB2	As	193.696	14.04	B.D.L.	ppm	3/6/97	22:38:36
1	1 CCB2	Al	396.152	14520	B.D.L.	ppm	3/6/97	22:38:48
1	1 CCB2	Mn	257.61	1199	B.D.L.	ppm	3/6/97	22:39:12
1	1 CCB2	Fe	259.94	1355	B.D.L.	ppm	3/6/97	22:39:35
1	1 CCB2	Mg	279.079	892.2	B.D.L.	ppm	3/6/97	22:39:54
1	1 CCB2	Ca	317.933	2891	B.D.L.	ppm	3/6/97	22:40:13

Section 9.3.1.				
Reagent Blank				
Acceptable Criteria		< 5 ppm		
	measured conc.			
sulfate	0.94	ppm		
Section 9.3.2.				
Lab Fortified Blank				
Recovery	90% - 110%			
	%R = 100 * (S-U)/C			
	Unspike (U)	Spike (S)	Actual conc.	R %
sulfate	1905	2816	937	97.225187
Section 9.3.4.				
Instrument Performance Check Solution				
Acceptable Criteria		10%		
	measured conc.	true value		%
sulfate	1066	1000	ppm	6.60
Section 9.3.4.				
Calibration Blank				
Acceptable Criteria		< 5 ppm		
	measured conc.			
sulfate	2.27	ppm		
Section 9.4.7.				
Field Duplicate				
RPD	<= 20%		RPD = 100 * (C1-C2)/[(C1+C2)/2]	
	C1	C2	RPD %	
sulfate	6923	7348	5.96	
	(sample 21)			

	Berkeley Pittlake water		
		sulfate (ppm)	%R
	unspike conc. (U)	8524	91.3
	spike conc. (S)	9437	
	actual conc. (C)	1000	
	Sample 12 (UV 254nm, Na-Formate)		
		sulfate (ppm)	%R
	unspike conc. (U)	8512	79.6
	spike conc. (S)	8308	
	actual conc. (C)	1000	
	Sample 13 (UV 254 nm, Hydrazine)		
		sulfate (ppm)	%R
	unspike conc. (U)	7750	97.7
	spike conc. (S)	8727	
	actual conc. (C)	1000	
	Sample 14 (UV 254 nm, TiO ₂)		
		sulfate (ppm)	%R
	unspike conc. (U)	8110	106.9
	spike conc. (S)	9179	
	actual conc. (C)	1000	
	Sample 15 (UV 254 nm, TiO ₂ & Na-Formate)		
		sulfate (ppm)	%R
	unspike conc. (U)	8066	76.8
	spike conc. (S)	8823	
	actual conc. (C)	1000	
	Sample 16 (UV 254 nm, TiO ₂ & Hydrazine)		
		sulfate (ppm)	%R
	unspike conc. (U)	6970	79.76331
	spike conc. (S)	7644	
	actual conc. (C)	845	
	Sample 20 (no-UV, Na-Formate)		
		sulfate (ppm)	%R
	unspike conc. (U)	8113	81.89349
	spike conc. (S)	8805	
	actual conc. (C)	846	
	Sample 21 (no-UV, Hydrazine)		
		sulfate (ppm)	%R
	unspike conc. (U)	6923	117.4746
	spike conc. (S)	7965	
	actual conc. (C)	887	